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The report describes a study of air pollutants released during the manufacture of chlorinated hydrocarbons, manufactured in the U.S. by: (1) direct chlorination (a hydrocarbon is reacted with chlorine); (2) hydrochlorination (hydrogen chloride is reacted with a hydrocarbon); (3) oxyhydrochlorination(hydrogen chloride is reacted with a hydrocarbon in the presence of oxygen or air); or (4) chlorohydrination (the reaction between a hydrocarbon and hydrochlorous acid is followed by a reaction of the products with lime slurry to obtain the final product). A representative plant was defined for each manufacturing process type, and environmental effects were determined on the basis of plant capacity. The potential environmental effect was evaluated using source severity, S, defined as the ratio of the maximum ground level concentration of an emission to the ambient air quality standard for criteria pollutants. Source severities for the four processes listed above are 1.69, 1.94, 31.3, and 2.75, respectively.

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Source Assessment: Chlorinated Hydrocarbons Manufacture

by

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PREFACE

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number (more than 500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to decide whether air emissions reduction is necessary for emissions from chlorinated hydrocarbons manufacture.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. D. A. Denny of IERL-RTP serves as EPA Project Officer. In this study of chlorinated hydrocarbons manufacture, Mr. Edward J. Wooldridge, Dr. I. Atly Jefcoat, and Mr. Bruce A. Tichenor served as EPA Task Officers.

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(Threshold Limit Value)

ABSTRACT

This report describes a study of air pollutants released during the manufacture of chlorinated hydrocarbons. The potential environmental effect of the source was evaluated using source severity, S, defined as the ratio of the maximum ground level concentration of an emission to the ambient air quality standard for criteria pollutants or to a modified TLV for noncriteria pollutants.

Chlorinated hydrocarbons are manufactured in the U.S. by one of four processes: 1) direct chlorination (a hydrocarbon is reacted with chlorine); 2) hydrochlorination (hydrogen chloride is reacted with a hydrocarbon); 3) oxyhydrochlorination (hydrogen chloride is reacted with a hydrocarbon in the presence of oxygen or air); and 4) chlorohydrination (the reaction between a hydrocarbon and hydrochlorous acid is followed by a reaction of the products with lime slurry to obtain the final product). In the U.S. during 1975, 32 companies with a total capacity of 11.5×10^6 metric tons/yr produced 8.52×10^6 metric tons of chlorinated hydrocarbons at 58 locations.

A representative plant was defined for each manufacturing process type, and the environmental effects were determined on the basis of capacity instead of production. Source severities for direct chlorination, hydrochlorination, oxychlorination, and chlorohydrination are 1.69, 1.94, 31.3, and 2.75, respectively.

Pollution control technology within the chlorinated hydrocarbon industry consists primarily of control of hydrocarbons emitted from the main process vent, product fractionating vent, storage tanks, fugitive sources, and waste disposal. Assuming that the same level of control will exist in 1980 as existed in 1975, air emissions from the industry are expected to increase by 20% over that period.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The study described in this report covers the period January 1976 to August 1978.

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ABBREVIATIONS AND SYMBOLS

A	--affected area
A_R	--factor defined as Q/acπu
AAQS	--ambient air quality standard
a,..e, v..z	--constants
B_R	--factor defined as $-H^2/2c^2$
C_i	--production capacity of plant i
$\overline{D}_P$	--(capacity weighted) mean population density
D_{P_i}	--county population·density for plant i
e	--constant; 2.72
exp	--natural log base, e
F	--hazard factor; for criteria pollutants, F is the primary ambient air quality standard; for noncriteria pollutants, F is a reduced TLV value, i.e., F = TLV • 8/24 • 1/100
H	--effective emission height
$K_1,..K_5$	--coefficients in overall stoichiometric equations
P	--total affected population
Q	--mass emission rate
S	--source severity
S_{CO}	--source severity for carbon monoxide emissions
S_{HC}	--source severity for hydrocarbon emissions
S_{NO_x}	--source severity for nitrogen oxide emissions
S_P	--source severity for particulate emissions
S_{SO_x}	--source severity for sulfur oxide emissions
t	--averaging time
t_o	--short-term averaging time
TLV	--threshold limit value
u	--wind speed

$\overline{u}$	--average wind speed
x	--downwind distance from source of emission
x_1, x_2	--roots of equation for affected area calculation
y	--horizontal distance from centerline of dispersion
z	--vertical distance from centerline of dispersion
π	--constant; 3.14
σ_y	--standard deviation of horizontal dispersion
σ_z	--standard deviation of vertical dispersion
χ	--downwind ground level concentration of a pollutant
$\overline{\chi}$	--average downwind ground level concentration of a pollutant
χ_{max}	--maximum ground level concentration of a pollutant
$\overline{\chi}_{max}$	--time-averaged maximum ground level concentration of a pollutant
$\overline{\chi}(x)$	--annual mean ground level concentration of a pollutant at a specific distance (x) from the source

SECTION I

INTRODUCTION

Fourteen major chlorinated hydrocarbons are included in this study, excluding pesticides and vinyl chloride, that have U.S. production capacities equal to or greater than 10^5 metric tons per year. Chlorinated hydrocarbons are principally used as solvents and chemical intermediates, in the manufactures of gasoline additives and chlorofluorocarbons for metal degreasing and cleaning, and in miscellaneous applications.

Four processes are currently used in the United States to manufacture chlorinated hydrocarbons: direct chlorination, hydrochlorination, oxyhydrochlorination, and chlorohydrination.

This document presents a detailed study of the chlorinated hydrocarbon industry from the standpoint of atmospheric emissions and their potential environmental impact. Major results of this study are summarized in Section II. Section III includes a brief description of the four chlorinated hydrocarbon manufacturing processes and the various compounds produced by each process. Included in the section are process chemistry, major processing steps, and block flow diagrams. Section IV discusses the types of material emitted from the unit operations of each manufacturing process, emission points, and the mass of material emitted. Several factors designed to measure the environmental hazard potential of chlorinated hydrocarbon manufacture are also determined. These consist of the source severity, the industry contribution to total atmospheric emissions of criteria pollutants, and the number of persons exposed to high contaminant levels from representative plants.

Section V reviews the current pollution control technology applicable to the control of atmospheric emissions from the manufacture of chlorinated hydrocarbons. The growth and nature of the industry are analyzed in Section VI.

SECTION II

SUMMARY

Chlorinated hydrocarbons are manufactured in the U.S. by one of four types of processes: direct chlorination, hydrochlorination, oxyhydrochlorination, and chlorohydrination. Direct chlorination represents 50% of the total chlorinated hydrocarbon capacity; hydrochlorination represents 11%; oxyhydrochlorination, 30%; and chlorohydrination, 9%. Chlorinated hydrocarbons considered for this study are those with annual production capacities more than 100,000 metric tons. During 1975 in the U.S., there were 32 companies with a total chlorinated hydrocarbon capacity of 11.5×10^6 metric tons/yr producing 8.52×10^6 metric tons of chlorinated hydrocarbons at 58 locations.

In the direct chlorination process, a hydrocarbon is reacted with chlorine. Hydrogen chloride is reacted with a hydrocarbon in the hydrochlorination process. In the oxyhydrochlorination process, hydrogen chloride is reacted with a hydrocarbon in the presence of oxygen (air). Chlorohydrination involves a reaction between a hydrocarbon and hydrochlorous acid and a further reaction of the products with lime slurry to obtain the final product. The products contained in the effluents from the reactor in all four processes are separated from byproducts and unreacted raw materials. This separation step is followed by distillation to obtain the pure product.

Major uses of chlorinated hydrocarbons are as solvents and chemical intermediates. They are also used in the manufacture of gasoline additives, chlorofluorocarbons, pesticides, and herbicides, and as solvents in drycleaning, cold cleaning, and vapor degreasing.

Sources of atmospheric emissions within a chlorinated hydrocarbon plant include the main process vent, product fractionation vent, storage tanks, fugitive sources, and waste disposal operations.

The potential hazard from the manufacture of chlorinated hydrocarbons was quantified by generating a number of factors, including: source severity, national and state burdens for criteria pollutants, affected population, and growth factor.

The source severity was defined as the ratio of the maximum time-averaged ground level concentration, determined by using Gaussian plume methodology, of a pollutant from a representative source to the hazard potential of the pollutant. The hazard potential for criteria pollutants is defined as the primary ambient air quality standard; for noncriteria pollutants, it is defined as a reduced threshold limit value (TLV®).

A representative plant was defined for each manufacturing process type. The parameters used to define the four representative plants include process type, population density, plant production rate, unit operations used, average emissions from specific unit operations, and emission rates for hydrocarbons. To depict a worst case analysis, capacities instead of production figures were used in all calculations.

For representative chlorinated hydrocarbon plants, emission rate and source severities for hydrocarbon emissions were determined to be:

Process	Hydrocarbon emission factor, g/kg	Hydrocarbon emission rate, g/s	Severity
Chlorination	2.78	6.88	1.69
Hydrochlorination	8.62	11.4	1.94
Oxyhydrochlorination	1.87	15.0	2.06
Chlorohydrination	123	480	46.8

The total mass of hydrocarbons emitted nationwide by the chlorinated hydrocarbon industry has been estimated to be 14,600 metric tons for the direct chlorination process, 9,950 metric tons for the hydrochlorination process, 62,000 metric tons for the oxyhydrochlorination process, and 120,000 metric tons for the chlorohydrination process. The percent contributions to national emissions are 0.06%, 0.04%, 0.024%, and 0.48% for the direct chlorination, hydrochlorination, oxyhydrochlorination, and chlorohydrination processes, respectively.

Statewide hydrocarbon emissions to the atmosphere from chlorinated hydrocarbon plants using the direct chlorination process are below 1.0% for Alabama, California, Delaware, Illinois, Indiana, Kansas, Kentucky, Louisiana, Maryland, Michigan, Nevada, New Jersey, New York, Ohio, Texas, and West Virginia. For the hydrochlorination process, statewide contributions range between 0.00% and 1.08% for California, Kansas, Kentucky, Louisiana, Michigan, New Jersey, New York, Texas, and West Virginia. For the oxyhydrochlorination process, state contributions to hydrocarbon emissions range between 0.014% and 0.26% for California, Texas, Kentucky and Louisiana.

For the chlorhydrination process, conbribtuions to state hydrocarbon emissions are 2.2% for Kentucky, 1.2% for Louisiana, 1.4% for Michigan, and 3.7% for Texas.

The average number of persons exposed to high contaminant levels from chlorinated hydrocarbons production was estimated and designated as the affected population. The calculation was made for total hydrocarbons emitted from all points within a representative plant for which the source severity exceeds 0.1. The affected populations were 2,820, 2,772, 4,580 and 297,600 for the direct chlorination, hydrochlorination, oxyhydrochlorination, and chlorohydrination processes, respectively.

The growth factor was determined from the ratio of known chlorinated hydrocarbon production in 1975 to projected production in 1980. Since 1975 production data and projected data for 1980 were unavailable for each process type, the growth factor was determined for the entire chlorinated hydrocarbon industry. Assuming that the same level of control will exist in 1980 as existed in 1975, emissions from the chlorinated hydrocarbon industry are expected to increase by 20% over that period; i.e.,

$$\frac{\text{Emissions in 1980}}{\text{Emissions in 1975}} = \frac{\text{Production in 1980}}{\text{Production in 1975}} = \frac{10.4 \times 10^6}{8.52 \times 10^6} = 1.2$$

Pollution control technology within the chlorinated hydrocarbon industry consists primarily of control of hydrocarbons emitted from the main process vent and product fractionating vent. Control techniques include absorption, condensation, incineration, and adsorption; and measures to control storage tank emissions, fugitive emissions, and emissions from waste disposal.

SECTION III

SOURCE DESCRIPTION

The chlorinated hydrocarbons source type is defined as those plants which currently produce the 14 chlorinated hydrocarbons listed in Table 1. All of those compounds listed have U.S. production capacities of 100,000 metric tons per year or more. One of the 14 compounds, propylene oxide, is not a chlorinated hydrocarbon, but it is included in this study because most of its U.S. production is accomplished by the chlorohydrination process using a chlorinated hydrocarbon as a chemical intermediate. Specifically excluded from the list are those chlorinated hydrocarbons which are classified as pesticides since these materials are the subject of an independent study. Vinyl chloride will also be separately studied and is not included in this document.

In 1975 there were 32 companies with a total capacity of 11.5×10^6 metric tons/yr producing 8.52×10^6 metric tons/yr of the 14 chlorinated hydrocarbons at 58 locations in the United States.[1-12]

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[1] Chemical Profile, Methyl Chloride. Chemical Marketing Reporter, 209(13):9, 1976.

[2] Chemical Profile, Methylene Chloride. Chemical Marketing Reporter, 210(12):9, 1976.

[3] Chemical Profile, Chloroform. Chemical Marketing Reporter, 210(13):9, 1976.

[4] Chemical Profile, Carbon Tetrachloride. Chemical Marketing Reporter, 207(22):9, 1975.

[5] Chemical Profile, Perchloroethylene. Chemical Marketing Reporter, 210(6):9, 1976.

[6] Chemical Profile, Phosgene. Chemical Marketing Reporter, 206(1):9, 1974.

[7] Chemical Profile, Monochlorobenzene. Chemical Marketing Reporter, 206(20):9, 1974.

[8] Chemical Profile, *p*-Dichlorobenzene. Chemical Marketing Reporter, 209(11):9, 1976.

(continued)

TABLE 1. CHLORINATED HYDROCARBONS WITH 1975 PRODUCTION CAPACITIES GREATER THAN 10^5 METRIC TONS/YR[1-12]

Product type	1975 Production capacity, 10^5 metric tons/yr	Percent of total chlorinated hydrocarbon capacity	1975 Production, 10^5 metric tons/yr	Percent of production	Percent of available capacity utilized	Estimated annual growth during 1975-1980, %	Estimated 1980 production, 10^5 metric tons/yr	Percent of estimated chlorinated hydrocarbon production in 1980
Ethylene dichloride	58.90	51.42	49.98	58.69	84.9	+4.0	60.81	58.7
Propylene oxide[a]	11.93	10.42	6.80	7.98	57.0	+10.5	11.20	10.8
Carbon tetrachloride	7.63	6.66	4.76	5.59	62.4	-10.0	2.81	2.7
Phosgene	7.22	6.30	4.41	5.18	61.1	+12.0	7.77	7.5
Perchloroethylene	5.01	4.37	3.16	3.71	63.1	+3.5	3.75	3.6
Ethyl chloride	3.86	3.37	2.61	3.06	67.6	-40.0	0.20	0.2
1,1,1-Trichloroethane	3.36	2.93	2.79	3.28	83.0	+4.0	3.39	3.3
Methylene Chloride	3.18	2.78	2.22	2.61	69.8	+11.0	3.74	3.6
Monochlorobenzene	3.13	2.73	1.76	2.07	56.2	+2.0	1.94	1.9
Methyl chloride	2.81	2.45	1.42	1.67	50.5	+6.0	1.90	1.8
Trichloroethylene	2.18	1.90	1.61	1.89	73.9	-8.0	1.06	1.0
Epichlorohydrin	2.04	1.78	1.71	2.01	83.8	+5.3	2.22	2.2
Chloroform	1.95	1.70	1.27	1.49	65.1	+9.0	1.95	1.9
Dichlorobenzene[b]	1.34	1.17	0.66	0.72	49.3	+3.5	0.78	0.8
Total[c,d]	114.54	99.98	85.16	99.95	74.3		103.52	100.00

[a] Propylene oxide is produced using two processes: 70% of the U.S. propylene oxide is produced from chlorohydrination of propylene while 30% is produced from peroxidation of propylene.

[b] Dichlorobenzene includes both *para*- and *ortho*-dichlorobenzenes.

[c] Total includes those product types having production capacities of 100,000 metric tons/year or more. Chlorinated hydrocarbons having production capacities less than 100,000 metric tons/year have not been included.

[d] Totals include rounding errors.

A. PROCESS DESCRIPTION

The production of chlorinated hydrocarbons can be categorized into four groups based on the four unit processes used during manufacture: (1) direct chlorination, (2) hydrochlorination, (3) oxyhydrochlorination, and (4) chlorohydrination. Direct chlorination represents 50% of the total chlorinated hydrocarbon capacity; hydrochlorination represents 11%; oxyhydrochlorination 30% and chlorohydrination 9%. A description of the four processes follows.

1. Direct Chlorination

Direct chlorination involves the reaction of a hydrocarbon with chlorine gas. The products and processes used to manufacture chlorinated hydrocarbons pertinent to this study are summarized in Table 2 together with the chemical equation representing each reaction.

TABLE 2. DIRECT CHLORINATION PROCESSES

Product	Manufacturing process	Chemical reactions	Equation No.
Methyl chloride	Direct chlorination of methane	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	1
Methylene chloride	Direct chlorination of methane	$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$	2
Chloroform	Direct chlorination of methane	$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$	3
Carbon tetrachloride	Direct chlorination of methane	$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$	4
Carbon tetrachloride	Direct chlorination of carbon disulfide	$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$	5
Carbon tetrachloride	Direct chlorination of propane	$C_3H_8 + 8Cl_2 \rightarrow CCl_4 + C_2Cl_4 + 8HCl$	6
Perchloroethylene	Direct chlorination of propane	$C_3H_8 + 8Cl_2 \rightarrow CCl_4 + C_2Cl_4 + 8HCl$	7
Ethylene dichloride	Direct chlorination of ethylene	$CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$	8
Phosgene	Direct chlorination of carbon monoxide	$CO + Cl_2 \rightarrow COCl_2$	9
Monochlorobenzene	Direct chlorination of benzene	$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$	10
Dichlorobenzene	Direct chlorination of benzene	$C_6H_6 + 2Cl_2 \rightarrow C_6H_4Cl_2 + 2HCl$	11

Table 2 indicates that a typical direct chlorination reaction can be represented by a general chemical reaction such as:

$$\text{Hydrocarbon} + \text{chlorine} \rightarrow \text{chlorinated hydrocarbon} + \text{hydrogen chloride} + (\text{byproduct}) \quad (12)$$

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[9] Chemical Profile, *o*-Dichlorobenzene. Chemical Marketing Reporter, 210(10):9, 1976.

[10] Chemical Profile, Trichloroethylene. Chemical Marketing Reporter, 208(12):9, 1975.

[11] Chemical Profile, Ethyl Chloride. Chemical Marketing Reporter, 210(13):9, 1976.

[12] Chemical Profile, Propylene Oxide. Chemical Marketing Reporter, 209(18):9, 1976.

The overall stoichiometric equation describing direct chlorination processes is:

$$C_vH_wCl_xO_yS_z + (K_1)Cl_2 \rightarrow C_aH_bCl_dO_e + (K_2)HCl + (K_3)S_2Cl_2 + (K_4)H_2O + (K_5)C_2Cl_4 \quad (13)$$

where $K_1 = \frac{1}{2}(2v + w - x - 2y + z - 2a - b + d + 2e)$

$K_2 = w - 2y - b + 2e$

$K_3 = \frac{1}{2}z$

$K_4 = y - e$

$K_5 = \frac{1}{2}(v - a)$

The direct chlorination process used in the manufacture of the above mentioned nine chlorinated hydrocarbons consists of three basic steps: (1) chlorination, (2) absorption, and (3) separation. Chlorination is carried out in a reactor, also called a chlorinator, where the hydrocarbon reacts with chlorine to produce the chlorinated hydrocarbon. The reaction is dependent on factors such as hydrocarbon used, catalyst used, reaction temperature, reactor space velocity, pressure, and the ratio of hydrocarbon to chlorine.

Effluents from the chlorinator include crude product, byproducts, unreacted raw materials, and catalyst. Effluents from the chlorinator are passed through an absorber, the second important section of the process, where they are condensed and where unreacted raw material is recovered. Hydrogen chloride formed during chlorination is now recovered from the system. Any remaining hydrogen chloride is neutralized in a neutralizer by scrubbing with caustic.

The crude product so obtained is then purified by separation, which can be carried out in one operation or a series of operations including fractional distillation, stripping, or phase separation. From the separator, the pure final chlorinated hydrocarbon, which has been separated from byproducts of the chlorination process, is withdrawn and sent to storage for sale or use.

a. Direct Chlorination of Methane--

Methyl chloride, methylene chloride, chloroform, and carbon tetrachloride are commercially produced by direct chlorination of methane.

(1) Chemistry--The basic chemical equations representing the chlorination of methane to methyl chloride, methylene chloride, chloroform, and carbon tetrachloride are:[13,14]

$$\mathrm{CH_4 + Cl_2 \rightarrow \underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(hydrogen chloride)}}{HCl}} \tag{14}$$

$$\mathrm{CH_3Cl + Cl_2 \rightarrow \underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(hydrogen chloride)}}{HCl}} \tag{15}$$

$$\mathrm{CH_2Cl_2 + Cl_2 \rightarrow \underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(hydrogen chloride)}}{HCl}} \tag{16}$$

$$\mathrm{CHCl_3 + Cl_2 \rightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(hydrogen chloride)}}{HCl}} \tag{17}$$

Raw materials used for the chlorination of methane are methane (99+%), chlorine (dry gas), caustic soda, sulfuric acid, and water. Products of the reaction are methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. Byproducts include hydrogen chloride, caustic sludge, and chlorinated heavy ends.[15] Copper and barium chlorides are used as catalysts. Yields for these reactions are between 85% to 90% based on methane.[13]

(2) Process--Figure 1 is a simple flow diagram for the chlorination of methane to produce methyl chloride, methylene chloride, chloroform, and carbon tetrachloride.[13-16,a] The reaction between chlorine and methane may be controlled so as to yield predominantly methyl chloride, with the formation of smaller amounts of methylene chloride, chloroform, and carbon tetrachloride. If methylene chloride is desired in largest amount, the methyl

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[13] Lowenheim, F. A., and M. K. Moran. Faith, Keyes, and Clark's Industrial Chemicals, Fourth Edition. John Wiley & Sons, Inc., New York, New York, 1975. 904 pp.

[14] Gruber, G. I. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries. EPA/530/SW-118C (PB 251 307), U.S. Environmental Protection Agency, Washington, D.C., April 1975. 377 pp.

[15] Air Pollution from Chlorination Processes. EPA Contract EPA 70-1, Task Order No. 23, U.S. Environmental Protection Agency, Office of Air Programs, March 31, 1972. 67 pp.

[16] Chloromethanes - Vulcan Materials Co. Hydrocarbon Processing, 54(11):127, 1975.

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[a] Some information provided by personal communication from T. H. Capps, Allied Chemical Company, Industrial Chemicals Division, Moundsville, West Virginia, July 28, 1976.

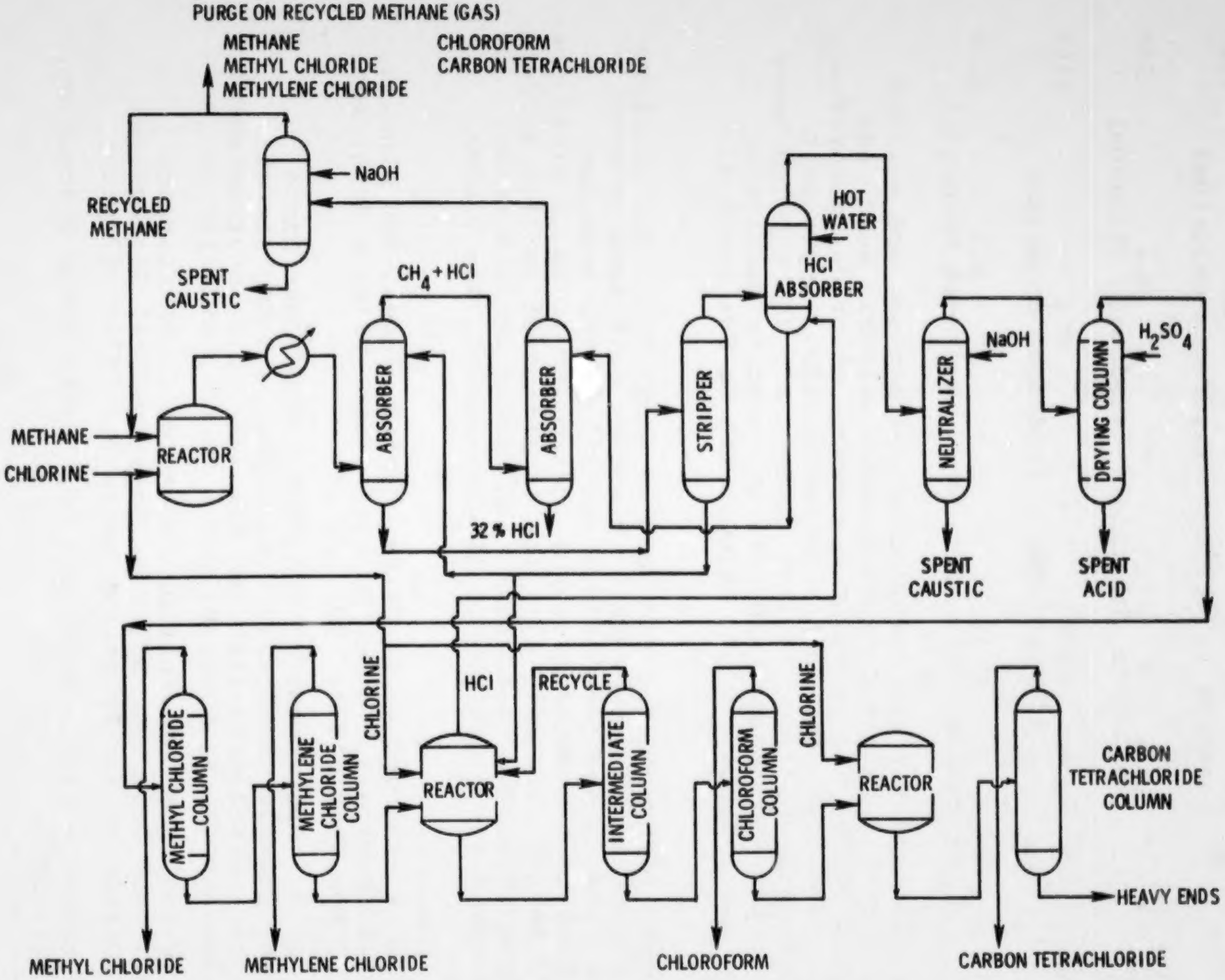
PURGE ON RECYCLED METHANE (GAS)
METHANE
METHYL CHLORIDE
METHYLENE CHLORIDE
CHLOROFORM
CARBON TETRACHLORIDE
NaOH
RECYCLED METHANE
SPENT CAUSTIC
CH$_4$ + HCl
HOT WATER
HCl ABSORBER
METHANE
CHLORINE
REACTOR
ABSORBER
ABSORBER
STRIPPER
NEUTRALIZER
NaOH
DRYING COLUMN
H$_2$SO$_4$
32 % HCl
SPENT CAUSTIC
SPENT ACID
METHYL CHLORIDE COLUMN
METHYLENE CHLORIDE COLUMN
CHLORINE
HCl
REACTOR
RECYCLE
INTERMEDIATE COLUMN
CHLOROFORM COLUMN
CHLORINE
REACTOR
CARBON TETRACHLORIDE COLUMN
HEAVY ENDS
METHYL CHLORIDE
METHYLENE CHLORIDE
CHLOROFORM
CARBON TETRACHLORIDE

Figure 1. Methyl chloride, methylene chloride, chloroform and carbon tetrachloride by the direct chlorination of methane.

chloride may be recycled to the chlorinator. Usually carbon tetrachloride is the most desired chloromethane, in which case most of the other chloromethanes are recycled.[13]

Methane is mixed with chlorine, preheated and fed to a reactor fitted with mercury arc lamps to promote the reaction at 350°C to 370°C and only slightly above atmospheric pressure and with residence times controlled so that the temperature desired may be held, chlorine is completely used up, and about 65% of the methane is reacted.[13] A typical range of products leaving the reactor is: methyl chloride - 58.5%; methylene chloride - 29.3%; chloroform - 9.7%; and carbon tetrachloride - 2.3%. The effluent gases from the reactor also contain unreacted methane and hydrogen chloride. These are separated from the chloromethanes by scrubbing the reacted gases with a mixture of liquid chloromethanes, usually a refrigerated mixture of chloroform and carbon tetrachloride. Methane and hydrogen chloride are not absorbed and go overhead. They are subsequently separated in a water absorber, and the methane recycled. The chloromethane absorbent, enriched with the chlorinated products removed from the reaction gases, is fed to a stripping column. Methyl chloride and some methylene dichloride go overhead. They are condensed and then purified by a hot water wash (to remove residual hydrogen chloride), an alkali wash, and a strong sulfuric acid wash (to dry the solvent mixture). The methyl chloride, methylene chloride, and any heavy ends are separated by fractional distillation.[13]

Not all the bottoms from the stripping column are recirculated to the reaction effluent absorber. A considerable portion of the liquid is fed to a secondary reactor, where more chlorine is added and a chlorination reaction is again carried out photochemically, but this time in the liquid phase. Hydrogen chloride is vented from the reactor. The reaction products are purified and separated by a sequence similar to that used for methyl chloride and methylene chloride, except that any product less chlorinated than chloroform is recycled. Desired quantities of chloroform are removed by distillation, and the remaining material is chlorinated in a third reactor to produce carbon tetrachloride.[13]

There is one source of air pollution. It is a purge on the recycled methane to remove inerts.[15]

b. Direct Chlorination of Carbon Disulfide--
Carbon tetrachloride is produced commercially by direct chlorination of carbon disulfide.

(1) Chemistry--The chemical reaction for the chlorination of carbon disulfide to produce carbon tetrachloride can be represented as:[13,17,18,a]

$$\underset{\text{(carbon disulfide)}}{CS_2} + \underset{\text{(chlorine)}}{3Cl_2} \rightarrow \underset{\text{(sulfur monochloride)}}{S_2Cl_2} + \underset{\text{(carbon tetrachloride)}}{CCl_4} \tag{18}$$

(sul

$$\underset{\text{(sulfur monochloride)}}{2S_2Cl_2} + \underset{\text{(carbon disulfide)}}{CS_2} \rightarrow \underset{\text{(sulfur)}}{6S} + \underset{\text{(carbon tetrachloride)}}{CCl_4} \tag{19}$$

$$\underset{\text{(sulfur)}}{6S} + \underset{\text{(carbon)}}{3C} \rightarrow \underset{\text{(carbon disulfide)}}{3CS_2} \tag{20}$$

Iron is used as the catalyst for the reaction. Yields are approximately 90% based on carbon disulfide.

(2) Process--In the direct chlorination process, carbon tetrachloride, carbon disulfide, and sulfur chlorides are contacted directly with excess chlorine at 30°C in the presence of divided iron catalyst.[15] Figure 2 is a simple block flow diagram for the direct chlorination of carbon disulfide to produce carbon tetrachloride.[15,a]

A slight excess of carbon disulfide feed is treated with sulfur monochloride in the primary reactor. Unconverted carbon disulfide is chlorinated in the chlorinator in the presence of divided iron catalyst. Effluents from the chlorinator reactor are distilled to separate crude product as overhead. Molten sulfur containing some sulfur monochloride is removed as bottoms. Sulfur equivalent to the fresh carbon disulfide feed is separated from the bottoms and returned to the carbon disulfide plant for processing. The residual sulfur stream is directly chlorinated in the sulfur chlorinator to form sulfur monochloride for the primary reactor.[15]

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[17] Austin, G. T. Industrially Significant Organic Chemicals, Part 3. Chemical Engineering, 81(6):87-92, 1974.

[18] Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 5. John Wiley & Sons, Inc., New York, New York, 1967. pp. 85-281.

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[a] Information also provided by personal communication from J. R. Hofts, FMC Corporation, South Charleston, West Virginia, November 10, 1076.

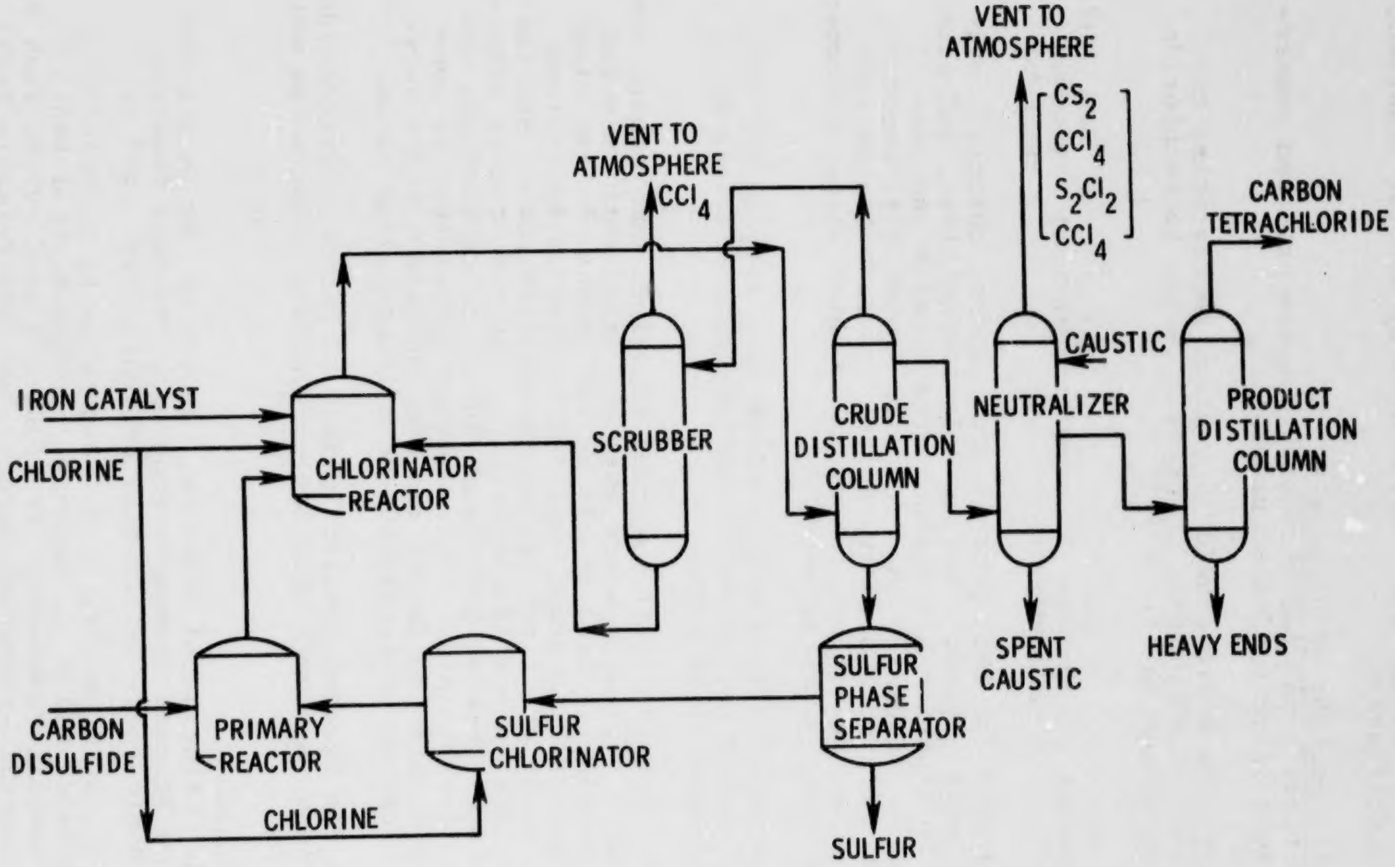
VENT TO ATMOSPHERE
CS_2
CCl_4
S_2Cl_2
CCl_4
VENT TO ATMOSPHERE
CCl_4
CARBON TETRACHLORIDE
CAUSTIC
IRON CATALYST
CHLORINE
CHLORINATOR REACTOR
SCRUBBER
CRUDE DISTILLATION COLUMN
NEUTRALIZER
PRODUCT DISTILLATION COLUMN
SPENT CAUSTIC
HEAVY ENDS
SULFUR PHASE SEPARATOR
CARBON DISULFIDE
PRIMARY REACTOR
SULFUR CHLORINATOR
CHLORINE
SULFUR

Figure 2. Carbon tetrachloride by the direct chlorination of carbon disulfide.

Overhead from the crude distillation column, consisting mainly of crude carbon tetrachloride, is purified by caustic treatment and product distillation.[15]

c. Direct Chlorination of Propane--
Carbon tetrachloride and perchloroethylene are produced commercially by direct chlorination of propane.

(1) Chemistry--The basic chemical equation representing the direct chlorination of propane to produce carbon tetrachloride and perchloroethylene is:[13,15,19,20]

$$\underset{\text{(propane)}}{C_3H_8} + \underset{\text{(chlorine)}}{8Cl_2} \rightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(perchloroethylene)}}{C_2Cl_4} + \underset{\text{(hydrogen chloride)}}{8HCl} \qquad (21)$$

Raw materials used for this process are propane, chlorine, sulfuric acid, copper chloride, barium chloride catalyst, and water. Products of the reaction are carbon tetrachloride and perchloroethylene. Yields for this reaction exceed 90%, based on propane.[13] The byproducts formed during the reaction include hexachlorobenzene, hexachloroethane, chlorinated waste, hydrogen chloride, and spent sulfuric acid.[13]

(2) Process--Figure 3 is a simple block flow diagram for the production of carbon tetrachloride and perchloroethylene by direct chlorination of propane.

Fresh chlorine, together with recycled chlorine, and propane are introduced into a vaporizer where they are mixed with recycled chlorides. Chlorine is used in 10% to 25% excess.[15] The mixed gases, at atmospheric pressure, are fed to a refractory-lined reactor. The gases are first heated to ignition point, and the reaction then takes place adiabatically. The temperature within the reactor ranges between 550°C and 700°C. After startup, the reaction is self-sustaining. The reaction temperature is controlled by the diluent action of recycled chlorides which serve to control the carbon tetrachloride/perchloroethylene ratio.[13,15]

Effluent from the reactor consists mainly of carbon tetrachloride, perchloroethylene, hydrogen chloride, and excess chlorine as well

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[19] Elkin, L. M. Chlorinated Solvents. Report No. 48 (a private report by the Process Economics Program), Stanford Research Institute, Menlo Park, California, February 1969. 377 pp.

[20] Hedley, W. H., S. M. Mehta, C. M. Moscowitz, R. B. Reznik, G. A. Richardson, and D. L. Zanders. Potential Pollutants from Petrochemical Processes. EPA Contract 68-02-0226, Task 9, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1973. 362 pp.

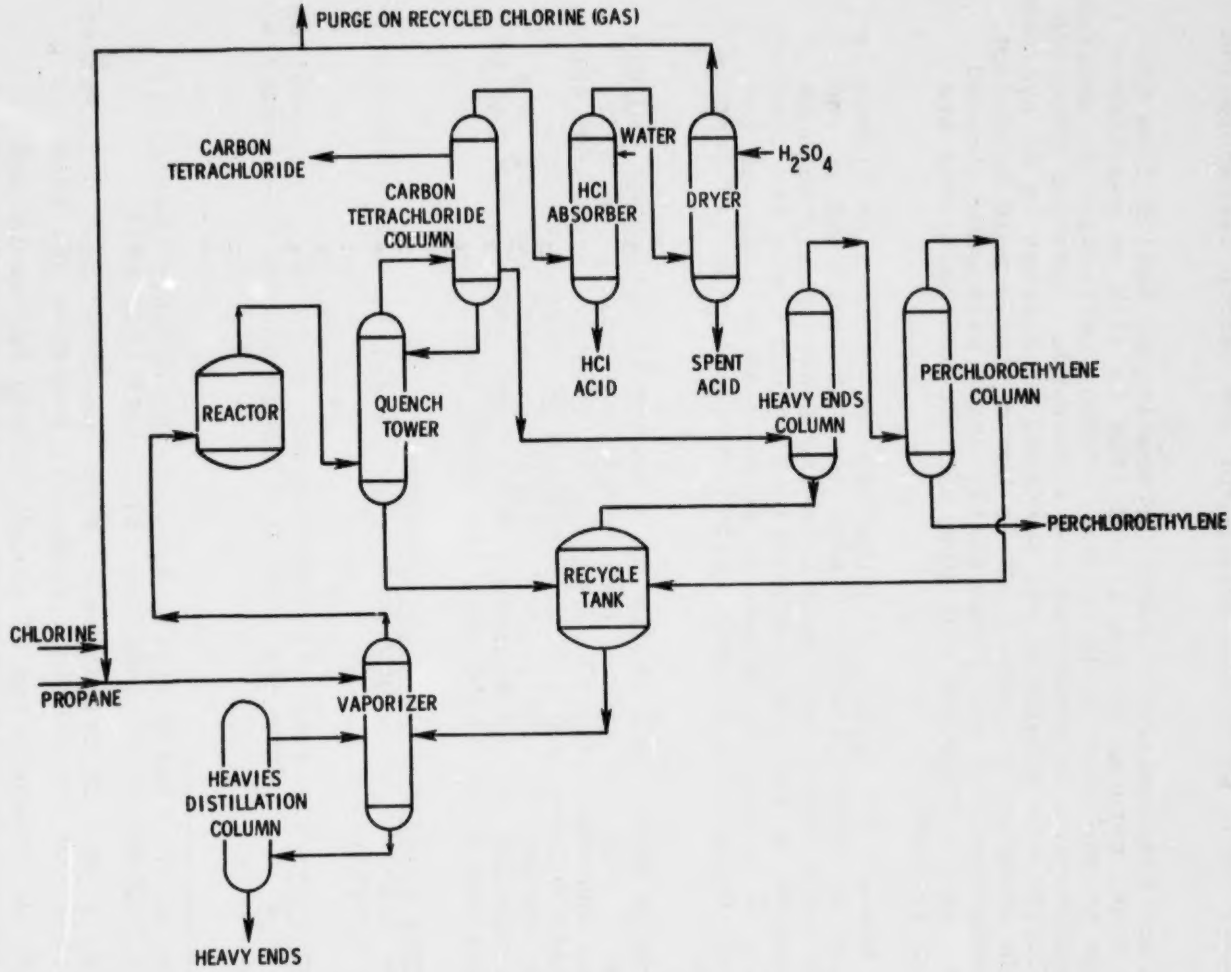
PURGE ON RECYCLED CHLORINE (GAS)
CARBON TETRACHLORIDE
CARBON TETRACHLORIDE COLUMN
HCl ABSORBER
WATER
DRYER
H_2SO_4
HCl ACID
SPENT ACID
REACTOR
QUENCH TOWER
HEAVY ENDS COLUMN
PERCHLOROETHYLENE COLUMN
PERCHLOROETHYLENE
RECYCLE TANK
CHLORINE
PROPANE
VAPORIZER
HEAVIES DISTILLATION COLUMN
HEAVY ENDS

Figure 3. Carbon tetrachloride and perchloroethylene by the direct chlorination of propane.[13,15]

as unreacted hydrocarbon. It is quenched by intimate contact with perchloroethylene to preserve the equilibrium ratio attained in the reactor, thereby preventing formation of undesirable byproducts. The hot effluent also serves to heat the contents of the quench tank, providing boilup for the carbon tetrachloride column.[15]

The carbon tetrachloride column, operating on boilup from the quench tank, returns bottom liquid that is rich in perchloroethylene to the heavy ends column. Carbon tetrachloride separated by fractionation is condensed and withdrawn. Hydrogen chloride and chlorine are separated and scrubbed with water in an hydrogen chloride absorber to remove HCl as hydrochloric acid byproduct. The noncondensables are subsequently dried with concentrated sulfuric acid. Chlorine and some uncondensed chlorides are recycled to feed.[15]

In the heavy ends column, the perchloroethylene-rich stream is distilled to remove the heavy ends that are returned to the recycle surge tank. Overhead from the heavy ends column is fractionated in the perchloroethylene column where the desired quantity of perchloroethylene is removed as bottoms and the overhead, containing largely carbon tetrachloride, is sent to recycle.[15]

The recycle surge tank serves as a reservoir for three recycle streams:[15] (1) the quench tank overflow (largely perchloroethylene and some hexachlorobenzene), (2) heavy ends from the heavy ends column, and (3) the perchloroethylene overhead (largely carbon tetrachloride). Proper control results in a recycle mixture of the desired composition, and this is fed to the vaporizer to be mixed with the fresh feed.[15]

d. Direct Chlorination of Ethylene--
Ethylene dichloride is produced commercially by direct chlorination of ethylene.

(1) Chemistry--The chemical reaction for the direct chlorination of ethylene to produce ethylene dichloride can be represented as follows:[13,15,20-24]

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[21] Austin, G. T. Industrially Significant Organic Chemicals, Part 5. Chemical Engineering, 81(9):143-150, 1974.

[22] Reilly, J. H. Chlorination of Ethylene Chloride. U.S. Patent 2,140,548 (to Dow Chemical Company), December 20, 1938. 1 p.

[23] Risbud, H. Description of Manufacturing Processes and Significant Air Emission Points at Ethyl Corporation Houston Plant. Region VI, Texas Air Control Board, Austin, Texas, August 1975. 18 pp.

(continued)

$$\underset{\text{(ethylene)}}{CH_2{=}CH_2} + \underset{\text{(chlorine)}}{Cl_2} \rightarrow \underset{\text{(ethylene dichloride)}}{ClCH_2CH_2Cl} \qquad (22)$$

Ethylene is chlorinated catalytically in a vapor- or liquid-phase reaction in the presence of ethylene dibromide as an anticatalyst against polychlorination at temperatures ranging between 50°C and 150°C and at 69 to 138 kPa gage (10 to 20 psig) pressure.[15,21] The catalysts used are metallic chlorides; e.g., ferric, aluminum, copper, or antimony.[13,15,22] Commercially, ferric chloride is employed as a catalyst in a liquid phase system. Yields are reported at approximately 90% based on ethylene theoretical.[13,15]

(2) Process--Figure 4 is a simple block flow diagram for the chlorination of ethylene to produce ethylene dichloride.[13,15,24] The composition of each process stream is shown in Table 3.[24] Chlorine is mixed with ethylene and fed to a reactor containing ethylene dibromide and ferric chloride catalyst. The reaction takes place in the liquid phase with an excess of reaction products. The reaction is exothermic (217.6 MJ/mole or 52 kcal/mole), and heat is removed by jacketed walls, internal cooling coils, or external heat exchange. A liquid and a vapor stream are obtained from the reactor.[13,24]

The overhead vapor effluent from the reactor is condensed in a water-cooled condenser or a refrigerated heat exchanger to condense any ethylene dichloride present in the vapor stream.[13,15,24] Noncondensables are sent through a scrubber to remove small amounts of hydrogen chloride and chlorine before venting to the atmosphere. Water or dilute caustic is used in the scrubber.[13,15,24]

Liquid effluent from the reactor consisting mainly of crude ethylene dichloride is cooled, then washed with a 6% to 8% caustic solution. Water is removed either by coalescing and phase separation or by phase separation and light ends distillation. Ethylene dichloride is obtained as overhead in a heavy ends distillation column. The bottoms comprised mainly of heavy ends is further separated into useful chlorinated hydrocarbons and tar.[13,15,24]

e. Direct Chlorination of Carbon Monoxide--
Phosgene is manufactured by direct chlorination of carbon monoxide.

(continued)

[24] Pervier, J. W., R. C. Barley, D. E. Field, B. M. Friedman, R. B. Morris, and W. A. Schwartz. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume II. EPA-450/3-73-005-b (PB 244 958), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1974. 332 pp.

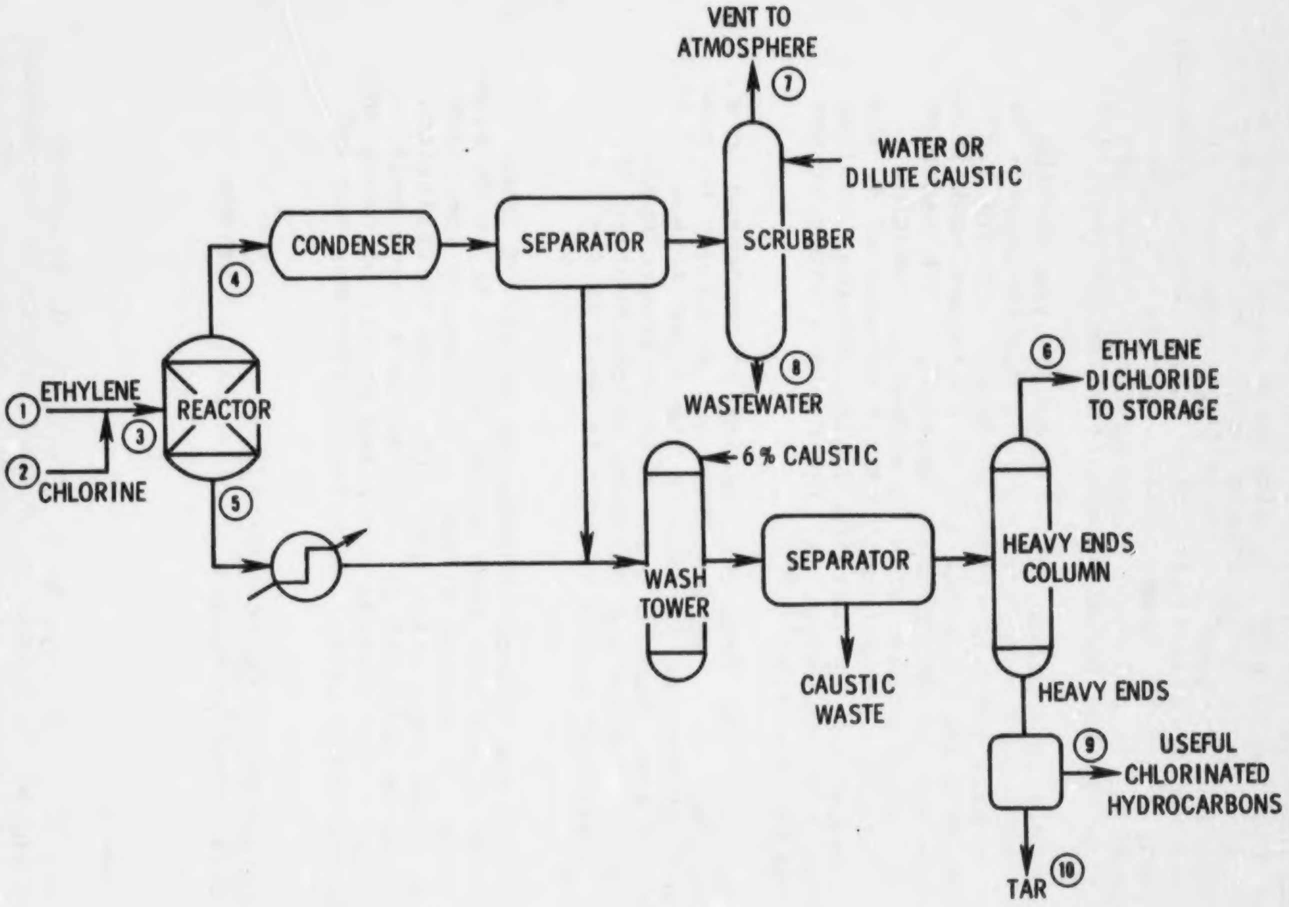
VENT TO ATMOSPHERE
⑦
WATER OR DILUTE CAUSTIC
SCRUBBER
CONDENSER
SEPARATOR
④
①
ETHYLENE
REACTOR
③
②
CHLORINE
⑤
⑧
WASTEWATER
⑥
ETHYLENE DICHLORIDE TO STORAGE
6 % CAUSTIC
WASH TOWER
SEPARATOR
CAUSTIC WASTE
HEAVY ENDS COLUMN
HEAVY ENDS
⑨
USEFUL CHLORINATED HYDROCARBONS
TAR
⑩

Figure 4. Ethylene dichloride by the direct chlorination of ethylene.[a],[13,15,24]

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[a] Composition of each stream is shown in Table 3.

TABLE 3. MATERIAL BALANCE FOR ETHYLENE DICHLORIDE BY DIRECT CHLORINATION OF ETHYLENE[24]
(kg/kg of product)

	Stream number[a]								
	1	2	3	4 and 5	6	7	8	9	10
Component	Ethylene feed	Chlorine feed	Total feed	Reactor effluent	Product	Scrubber vent	Acid, chlorine, and ethylene dichloride in scrubber waste	Useful heavy ends	Tar
Ethylene	0.2916		0.2916	0.0031		0.0031			
Chlorine		0.7258	0.7258	0.0001			0.0001		
Inerts									
CO_2		0.0040	0.0040	0.0040		0.0040			
O_2		0.0087	0.0087	0.0087		0.0087			
N_2		0.0076	0.0076	0.0076		0.0076			
H_2		0.0002	0.0002	0.0002		0.0002			
Ethylene dichloride				1.0030	0.9990	0.0022	0.0018		
Ethylene trichloride				0.0101	0.0010			0.0091	
Hydrogen chloride				0.0004			0.0004		
Tar				0.0007					0.0007
TOTAL	0.2916	0.7463	1.0379	1.0379	1.0000	0.0258	0.0023	0.0091	0.0007

[a] Stream numbers are indicated in Figure 4.

NOTE: Blanks indicate component not present in stream.

(1) Chemistry--The chemical reaction for the chlorination of carbon monoxide to produce phosgene can be represented as follows:[25-27]

$$\underset{\text{(carbon monoxide)}}{CO} + \underset{\text{(chlorine)}}{Cl_2} \xrightarrow{\text{activated charcoal}} \underset{\text{(phosgene)}}{COCl_2} \qquad (23)$$

There are no byproducts formed during this reaction, and yields are approximately 99% based on carbon monoxide.[15,25]

(2) Process--Figure 5 is a simple block flow diagram for the chlorination of carbon monoxide to produce phosgene.[13,15,a] Carbon monoxide and chlorine are separately dried, filtered, and fed into the chlorinator reactor. Temperature within the reactor is approximately 200°C, and pressure is 14 to 28 kPa gage (2 to 4 psig).[13,15,25] The reactor is equipped with water-cooled tubes and is filled with activated charcoal. The reaction is very rapid and exothermic. Efficient heat removal is important to avoid reversion of phosgene into its raw materials.

Reactor effluents flow into a condenser where liquid phosgene is separated from the system. Noncondensables are sent to an absorber where toluene or benzene serves as a solvent for the removal of final traces of phosgene. Phosgene is separated from the solvent in the solvent still and is recycled back to the condenser.[13]

f. Direct Chlorination of Benzene--
Monochlorobenzene and *para-* and *ortho-*dichlorobenzenes are produced commercially by direct chlorination of benzene.

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[25] Austin, G. T. Industrially Significant Organic Chemicals, Part 8. Chemical Engineering, 81(15):107-116, 1974.

[26] Lord, A., and H. O. Pritchard. Thermodynamics of phosgene formation from carbon monoxide and chlorine. Journal of Chemical Thermodynamics, 2(2):187-191, 1970.

[27] Shreve, R. N. The Chemical Process Industries. 3rd Edition. McGraw Hill Book Company, Inc., New York, New York, 1967. 905 pp.

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[a] Information also provided by personal communication with R. A. Coates, Mobay Chemical Company, New Martinsville, West Virginia, April 1, 1976.

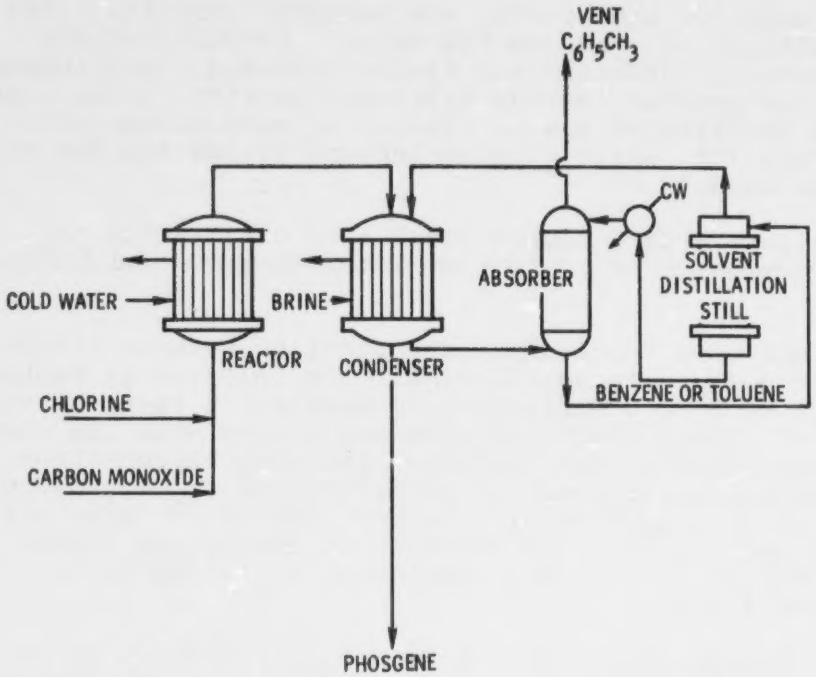
VENT
$C_6H_5CH_3$
CW
ABSORBER
SOLVENT DISTILLATION STILL
COLD WATER
BRINE
REACTOR
CONDENSER
BENZENE OR TOLUENE
CHLORINE
CARBON MONOXIDE
PHOSGENE

Figure 5. Phosgene by the direct chlorination of carbon monoxide.

(1) Chemistry--The basic chemical equations representing the chlorination of benzene to produce monochlorobenzene and dichlorobenzene are:[13-15,18,28,29]

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(chlorine)}}{Cl_2} \xrightarrow{20°C\text{ to }60°C} \underset{\text{(monochlorobenzene)}}{C_6H_5Cl} + \underset{\text{(hydrogen chloride)}}{HCl} \qquad (24)$$

$$\underset{\text{(monochlorobenzene)}}{C_6H_5Cl} + \underset{\text{(chlorine)}}{Cl_2} \rightarrow \underset{\text{(dichlorobenzene)}}{C_6H_4Cl_2} + \underset{\text{(hydrogen chloride)}}{HCl} \qquad (25)$$

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[28] Sittig, M. Pollution Control in the Organic Chemical Industry. Noyes Data Corporation, Park Ridge, New Jersey, 1974. 304 pp.

[29] Austin, G. T. Industrially Significant Organic Chemicals, Part 7. Chemical Engineering, 81(13):149-156, 1974.

Raw materials used for the process are benzene, chlorine, iron turnings as catalyst, and sodium hydroxide. Products of the reaction are monochlorobenzene and dichlorobenzene. Byproducts formed during the process include hydrogen chloride, spent caustic sludge and chlorinated waste. Yields of monochlorobenzene are approximately 75%, while dichlorobenzene yields are 10% to 20% based on benzene.[15]

(2) Process--Figure 6 is a simple block flow diagram for the chlorination of benzene to produce monochlorobenzene and dichlorobenzene.[13-15,29]

Iron turnings are used to catalyze the reaction between liquid phase dry benzene and gaseous chlorine. The chlorine is bubbled into the charge at a rate sufficient to maintain a temperature at 40°C to 60°C. The product distribution varies with the quantity of chlorine added to the reactors; for monochlorobenzene only, the chlorination temperature is maintained at about 40°C and about 60% of the theoretical chlorine used.[13,15] When all the benzene is chlorinated, the reaction is run at the higher temperature (55°C to 60°C) and a density of 1.280 (15°C) is reached in about 6 hours.

The hydrogen chloride produced is scrubbed with benzene or chlorobenzene to remove entrained organics and is absorbed in water to produce commercial-grade hydrochloric acid. Vent gas from the absorber/scrubber contains a small amount of residual HCl.[13,15]

Product crude chlorobenzene from the reactor kettle is agitated in a steam-jacketed neutralizer with warm dilute (10%) sodium hydroxide solution to remove residual acidity. After neutralization, the bulk of the dichlorobenzene is retained in the sludge which is sent for recovery by distillation. Supernatant liquor from the separator is sent to fractionating towers for recovery of benzene, monochlorobenzene, and dichlorobenzene.[13,14] If the chlorination is carried out so that the theoretical quantity of chlorine is consumed (100% chlorination), the following fractions are obtained in approximately the indicated percentages:

	Percent
Benzene and water	3
Benzene and chlorobenzene	10
Chlorobenzene	75
Chlorobenzene and dichlorobenzenes	10
Resinous materials and loss	2

The first two fractions are returned to the system for further processing, and the third (chlorobenzene) is run to storage. The fourth fraction is allowed to accumulate and is then distilled. The para isomer is collected in the distillate; the residue contains the ortho isomer contaminated with some para isomer and polychlorobenzenes, principally 1,2,4-trichlorobenzene. Of the

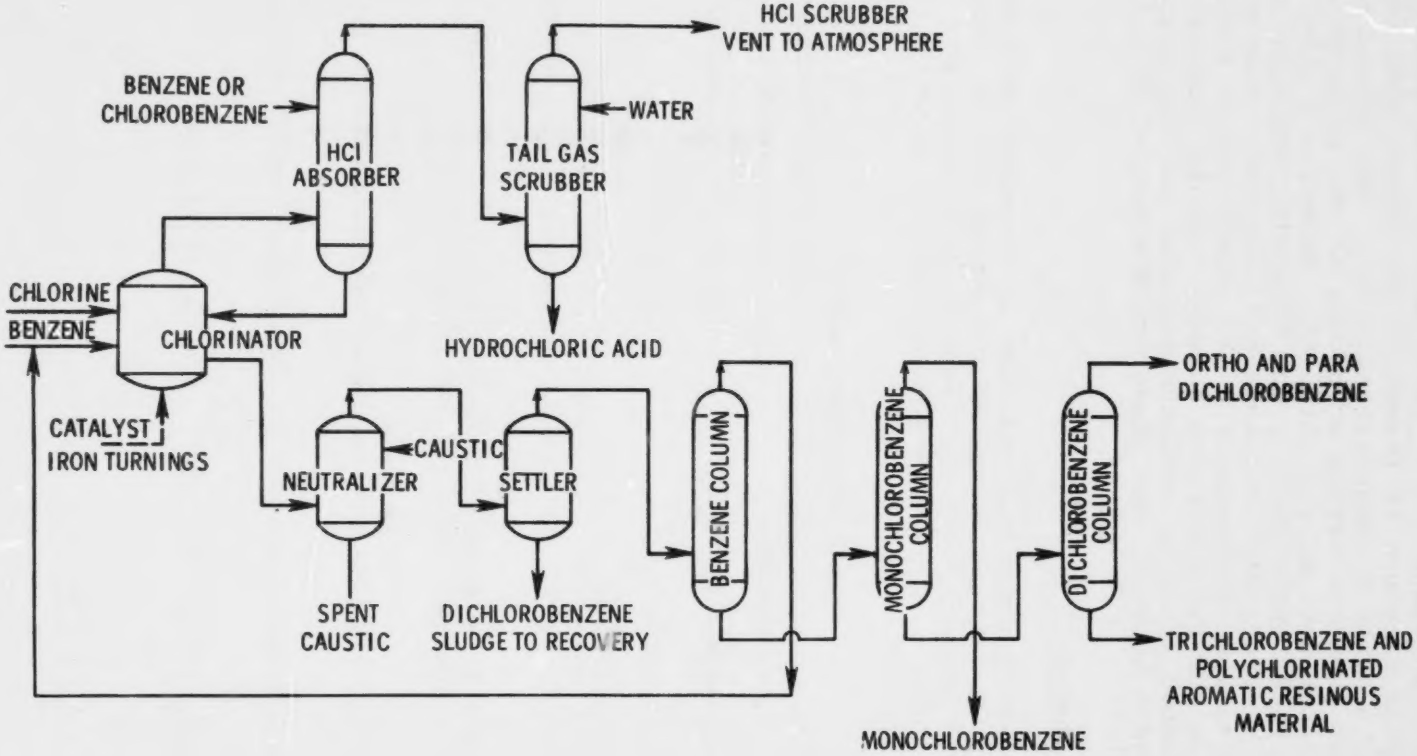
HCl SCRUBBER
VENT TO ATMOSPHERE
BENZENE OR
CHLOROBENZENE
HCl
ABSORBER
TAIL GAS
SCRUBBER
WATER
CHLORINE
BENZENE
CHLORINATOR
HYDROCHLORIC ACID
CATALYST
IRON TURNINGS
CAUSTIC
NEUTRALIZER
SETTLER
BENZENE COLUMN
MONOCHLOROBENZENE
COLUMN
DICHLOROBENZENE
COLUMN
ORTHO AND PARA
DICHLOROBENZENE
SPENT
CAUSTIC
DICHLOROBENZENE
SLUDGE TO RECOVERY
TRICHLOROBENZENE AND
POLYCHLORINATED
AROMATIC RESINOUS
MATERIAL
MONOCHLOROBENZENE

Figure 6. Monochlorobenzene and dichlorobenzene by the direct chlorination of benzene.[13,15,29]

two isomeric dichlorobenzenes, (practically no meta isomer formed), the para compound is formed in the larger quantity; the ratio of para to ortho is approximately 3:1. The composition of the chlorinated products varies according to the chlorination temperature, rate, degree, and catalyst. However, a 100% chlorination will yield approximately the following composition: chlorobenzene - 80%; *p*-dichlorobenzene - 15%; and *o*-dichlorobenzene including polychlorobenzenes - 5%. Distillation residues discharged from the fractionating columns contain about 0.04 kg of polychlorinated aromatic resinous material per kilogram of monochlorobenzene product, and these are discharged to solid waste disposal.[14]

2. Hydrochlorination

Hydrochlorination involves the reaction of a hydrocarbon with hydrogen chloride. The products and processes used to manufacture chlorinated hydrocarbons pertinent to this study are summarized in Table 4 together with the chemical equation representing each reaction.

TABLE 4. HYDROCHLORINATION PROCESSES

Product	Manufacturing process	Chemical reactions	Equation No.
Methyl chloride	Hydrochlorination of methanol	$CH_3OH + HCl \xrightarrow[\text{liquid phase}]{\text{catalyst}} CH_3Cl + H_2O$	26
Ethyl chloride	Hydrochlorination of ethylene	$C_2H_4 + HCl \xrightarrow{\text{catalyst}} C_2H_5Cl$	27
1,1,1-Trichloroethane	Hydrochlorination of vinyl chloride (by hydrochlorination, then chlorination)	$CH_2{=}CHCl + HCl \xrightarrow{\text{catalyst}} C_2H_4Cl_2$ $C_2H_4Cl_2 + Cl_2 \rightarrow CH_3CCl_3 + HCl$	28 29

As shown in Table 4, a typical hydrochlorination reaction can be represented by a general chemical equation such as:

$$\text{Hydrocarbon + hydrogen chloride} \xrightarrow{\text{catalyst}} \text{chlorinated hydrocarbon + (byproducts)} \qquad (30)$$

The overall stoichiometric equation describing hydrochlorination processes is:

$$C_xH_yCl_zO_w + (K_1)HCl \rightarrow C_aH_bCl_d + (K_2)H_2O \qquad (31)$$

where $K_1 = d - z$

$$K_2 = \frac{d + y - z - b}{2}$$

The hydrochlorination process used in the manufacture of the above-mentioned three chlorinated hydrocarbons consists of three basic steps: (1) hydrochlorination, (2) absorption, and (3) separation.

Chlorinated hydrocarbons are formed by the reaction of the hydrocarbon and hydrogen chloride in the presence of a catalyst. The reaction depends on various factors including hydrocarbon used, catalyst used, reaction temperature and pressure, and the ratio of hydrocarbon to hydrogen chloride. Effluents from the hydrochlorinator reactor include crude product, byproducts, unreacted raw materials, and catalyst.

The second step of the hydrochlorination process is absorption. Reactor effluents are passed through an absorber to condense and recover unreacted raw materials. Hydrogen chloride not removed in the absorber is neutralized by scrubbing with caustic.

The third step of the process is fractional distillation where the product is separated from the byproducts and waste. Separation can be one operation or a series of operations, including stripping, decanting, or distillation. The final product is withdrawn and sent to storage.

a. Hydrochlorination of Methanol--
Chloromethanes are manufactured by hydrochlorination of methanol.

(1) Chemistry--The chemical reaction for the hydrochlorination of methanol to produce methyl chloride can be represented as follows:[13-15,17,28]

$$\underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(hydrochloric acid)}}{HCl} \xrightarrow[\text{liquid phase (340°C)}]{\text{catalyst}} \underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(water)}}{H_2O} \tag{32}$$

Zinc chloride on pumice, cuprous chloride, or activated charcoal is used as catalyst. Yield for the reaction is 90% to 95%, based on methanol.[17]

(2) Process--Figure 7 is a simple block flow diagram for the hydrochlorination of methanol to produce methyl chloride.[13-15] During startup operation, the plant uses an external supply of HCl to react with methanol to produce methyl chloride. Subsequently, the plant generates the hydrogen chloride needed via the reaction of chlorine with methyl chloride and with methyl chloride chlorination products recycled from the various purification towers. Reactions occurring in the thermal chlorinator are:[14,15,17,28]

$$\underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(chlorine)}}{Cl_2} \rightarrow \underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(hydrochloric acid)}}{HCl} \tag{33}$$

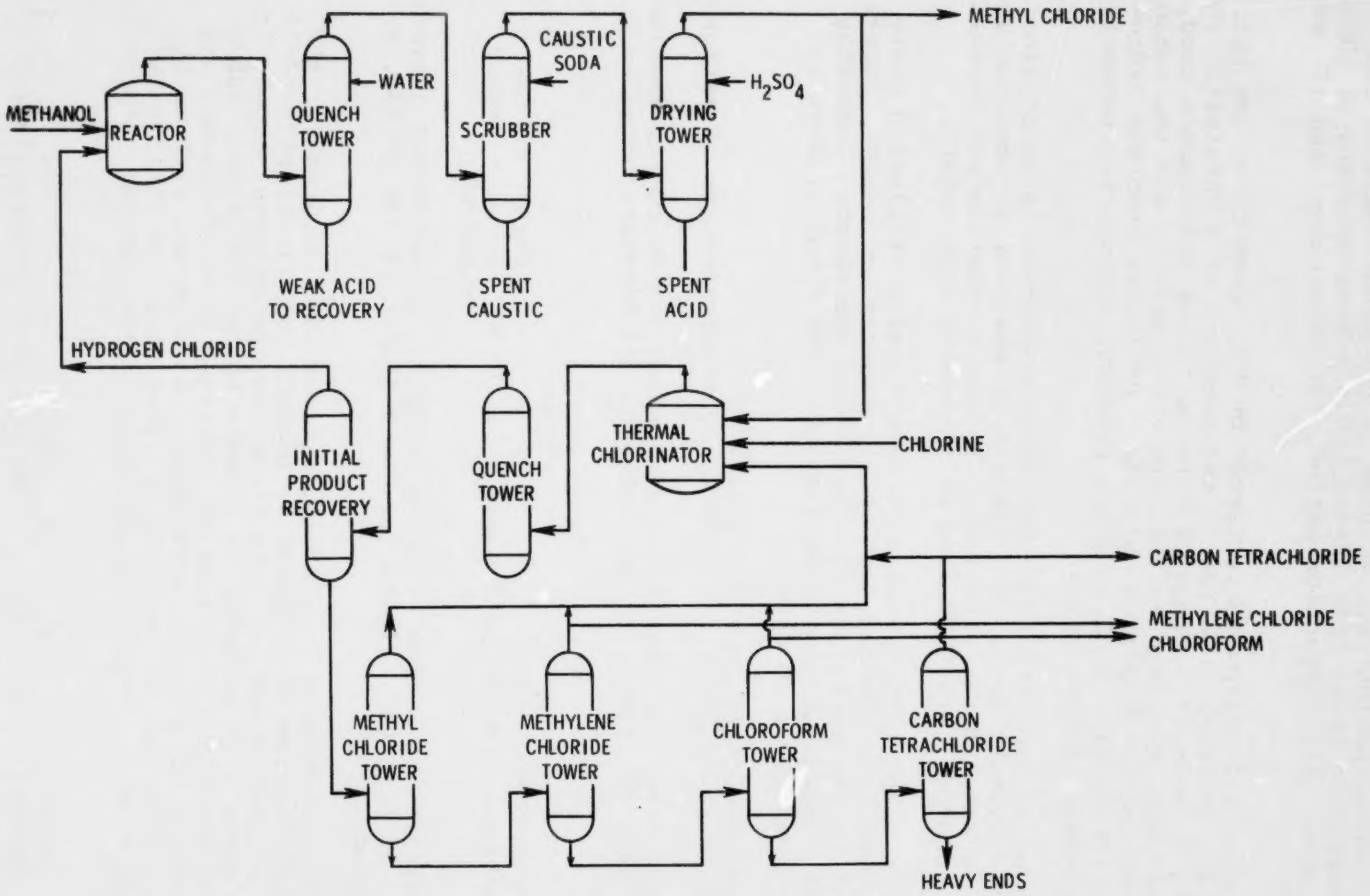
METHANOL
REACTOR
QUENCH TOWER
WATER
WEAK ACID TO RECOVERY
SCRUBBER
CAUSTIC SODA
SPENT CAUSTIC
DRYING TOWER
H_2SO_4
SPENT ACID
METHYL CHLORIDE
HYDROGEN CHLORIDE
INITIAL PRODUCT RECOVERY
QUENCH TOWER
THERMAL CHLORINATOR
CHLORINE
CARBON TETRACHLORIDE
METHYLENE CHLORIDE
CHLOROFORM
METHYL CHLORIDE TOWER
METHYLENE CHLORIDE TOWER
CHLOROFORM TOWER
CARBON TETRACHLORIDE TOWER
HEAVY ENDS

Figure 7. Methyl chloride by the hydrochlorination of methanol.[14,15]

$$\underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(chlorine)}}{Cl_2} \rightarrow \underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(hydrochloric acid)}}{HCl} \tag{34}$$

$$\underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(chlorine)}}{Cl_2} \rightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(hydrochloric acid)}}{HCl} \tag{35}$$

The excess hydrogen chloride produced in the reaction is separated, dried, compressed, and sold as anhydrous HCl.

Hydrogen chloride and methanol react in the liquid phase in the presence of a catalyst to produce methyl chloride. The methyl chloride vapor phase is quenched, washed with caustic soda solution to remove traces of hydrogen chloride, and dried with sulfuric acid prior to transfer as a liquid to product storage.[13,14]

The weak acid produced in the quench tower is fortified with hydrogen chloride gas and sold as commercial hydrochloric acid. Spent caustic solution and spent sulfuric acid "bleeds" are neutralized and discharged to the water treatment facilities.[14]

Mixed chloromethanes formed in the thermal chlorinator reactor after separation of hydrogen chloride are fractionated to recover the chlorinated hydrocarbon solvents. A portion of the methyl chloride, methylene chloride, and chloroform from the fractionation towers is recycled to produce hydrogen chloride. The remainder is sent to storage as product. Carbon tetrachloride after rectification goes to storage as product. Heavy ends composed of higher chlorinated hydrocarbons (predominantly crude hexachlorobenzene and hexachlorobutadiene) are sent to the waste disposal system.[14]

b. Hydrochlorination of Ethylene--
Ethyl chloride is manufactured by hydrochlorination of ethylene.

(1) Chemistry--The chemical reaction for the hydrochlorination of ethylene to produce ethyl chloride can be represented as follows:[13-15,21,28]

$$\underset{\text{(ethylene)}}{C_2H_4} + \underset{\text{(hydrochloric acid)}}{HCl} \xrightarrow[35^\circ C \text{ to } 40^\circ C]{AlCl_3} \underset{\text{(ethyl chloride)}}{C_2H_5Cl} \tag{36}$$

Anhydrous hydrogen chloride, in the presence of aluminum chloride, reacts with ethylene in both liquid and vapor phases to give 90% to 95% yields of ethyl chloride based on ethylene[13,14,21] Yields of polychloro compounds are reduced by the addition of ethylene dichloride to the reaction mixture.[14]

(2) Process--Figure 8 is a simple block flow diagram for the hydrochlorination of ethylene to produce ethyl chloride. This continuous hydrochlorination process accounts for 88% of ethyl chloride production.[13-15,21]

Ethylene gas and hydrogen chloride from storage tanks are fed to a mixer where equimolar quantities are combined. The gaseous mixture is fed to a reactor partially filled with ethylene dichloride. Temperature within the reactor ranges between 40°C and 45°C, and the pressure is 277 kPa gage (40 psig). Under these conditions and in the presence of aluminum chloride catalyst, the exothermic hydrochlorination of ethylene to produce ethyl chloride takes place.[13-15]

Vaporized products from the reactor include ethyl chloride, hydropolymer oil, and miscellaneous chlorinated hydrocarbons. Effluents from the reactor are sent to a separator where the hydropolymer oil (0.02 kg per kg of ethyl chloride) is separated to be sold as byproducts. Crude ethyl chloride is refined by fractionation. Chlorinated hydrocarbon tails, obtained as bottoms (0.093 kg per kg of ethyl chloride), are sent to chlorinated solvent manufacturers. Ethylene dichloride detained in the fractionation column is recycled back to the reactor. Pure ethyl chloride obtained as overhead in the fractionator is sent to storage.[14]

c. Hydrochlorination of Vinyl Chloride--

Hydrochlorination of vinyl chloride followed by direct chlorination is commercially used for the manufacture of 1,1,1-trichloroethane.

(1) Chemistry--The chemical reactions for the hydrochlorination and chlorination of vinyl chloride to produce 1,1,1-trichloroethane can be represented as follows:[13-15]

$$\underset{\text{(vinyl chloride)}}{CH_2{=}CHCl} + \underset{\text{(hydrogen chloride)}}{HCl} \xrightarrow[\text{35°C to 40°C}]{FeCl_3} \underset{\text{(dichloroethane)}}{C_2H_4Cl_2} \tag{37}$$

$$\underset{\text{(dichloroethane)}}{C_2H_4Cl_2} + \underset{\text{(chlorine)}}{Cl_2} \xrightarrow[\text{400°C}]{} \underset{\text{(1,1,1-trichloroethane)}}{CH_3CCl_3} + \underset{\text{(hydrogen chloride)}}{HCl} \tag{38}$$

The yield is 95% based on vinyl chloride in the presence of ferric chloride catalyst.[13]

(2) Process--Figure 9 is a simple block flow diagram for the hydrochlorination and chlorination of vinyl chloride to produce 1,1,1-trichloroethane.[13-15,19]

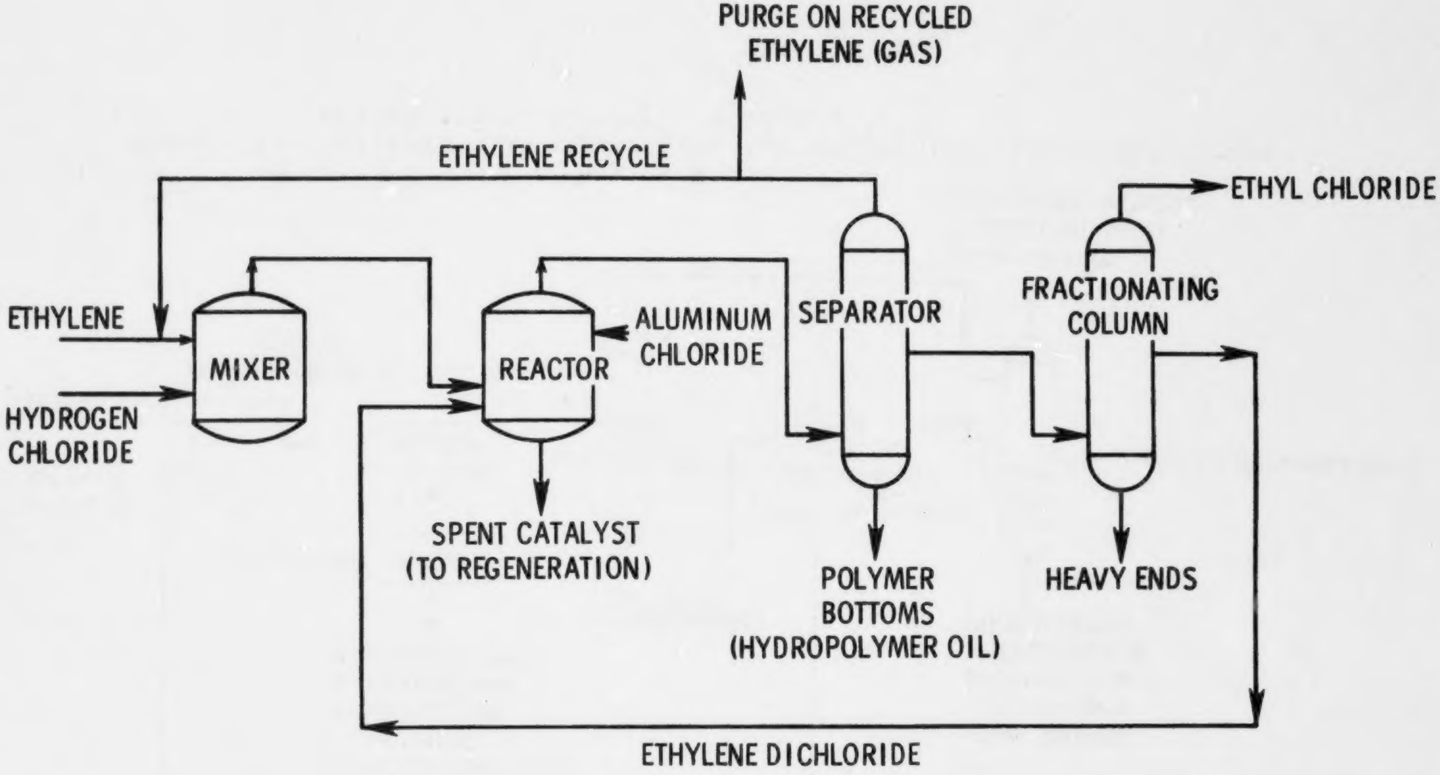
PURGE ON RECYCLED ETHYLENE (GAS)
ETHYLENE RECYCLE
ETHYL CHLORIDE
ETHYLENE
HYDROGEN CHLORIDE
MIXER
REACTOR
ALUMINUM CHLORIDE
SEPARATOR
FRACTIONATING COLUMN
SPENT CATALYST (TO REGENERATION)
POLYMER BOTTOMS (HYDROPOLYMER OIL)
HEAVY ENDS
ETHYLENE DICHLORIDE

Figure 8. Ethyl chloride by the hydrochlorination of ethylene.[13,15-21]

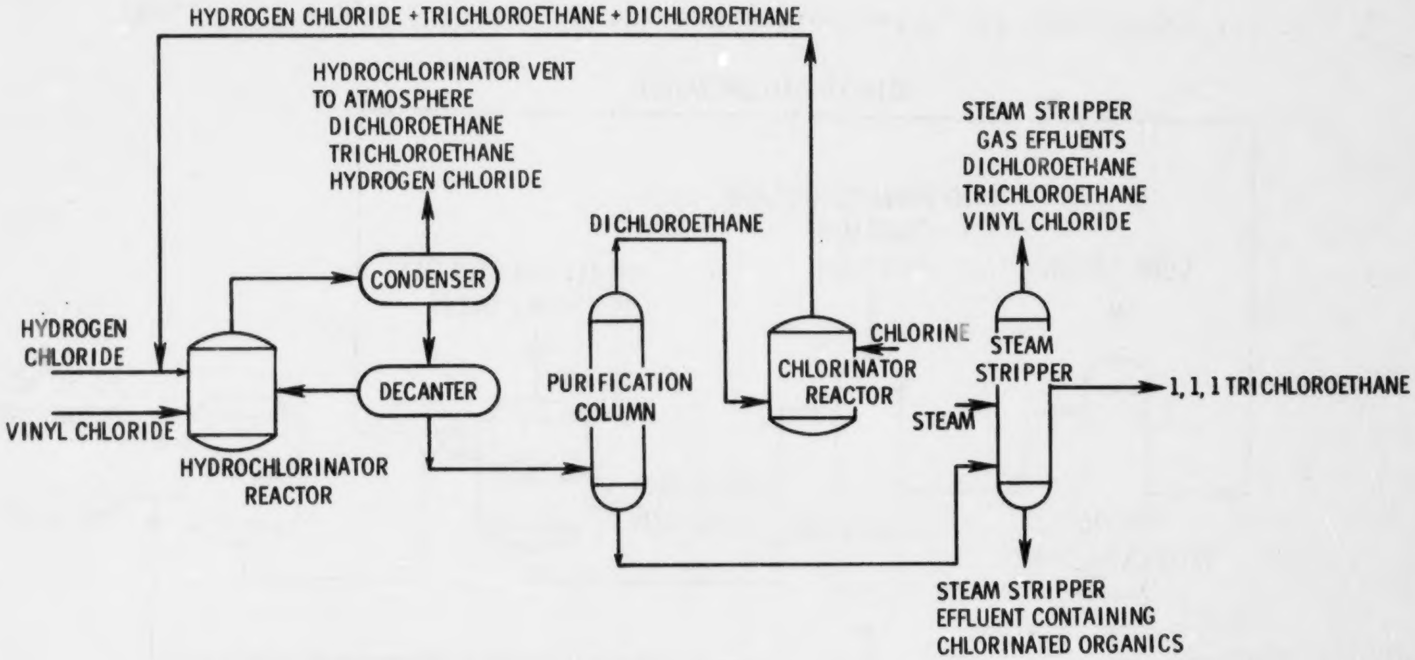
HYDROGEN CHLORIDE + TRICHLOROETHANE + DICHLOROETHANE
HYDROCHLORINATOR VENT
TO ATMOSPHERE
DICHLOROETHANE
TRICHLOROETHANE
HYDROGEN CHLORIDE
STEAM STRIPPER
GAS EFFLUENTS
DICHLOROETHANE
TRICHLOROETHANE
VINYL CHLORIDE
DICHLOROETHANE
CONDENSER
HYDROGEN
CHLORIDE
CHLORINE
STEAM
STRIPPER
DECANTER
PURIFICATION
COLUMN
CHLORINATOR
REACTOR
1, 1, 1 TRICHLOROETHANE
STEAM
VINYL CHLORIDE
HYDROCHLORINATOR
REACTOR
STEAM STRIPPER
EFFLUENT CONTAINING
CHLORINATED ORGANICS

Figure 9. 1,1,1-Trichloroethane by the hydrochlorination and direct chlorination of vinyl chloride.[13,15]

Vinyl chloride, makeup and recycled hydrogen chloride, recycled dichloroethane, and recycled trichloroethane are fed to a tower reactor for the catalyzed hydrochlorination reaction, which produces the dichloroethane intermediate. The hydrochlorination reaction takes place at 35°C to 40°C in the presence of ferric chloride catalyst.[13-15]

Dichloroethane, obtained as overhead from the purification column, is chlorinated in the chlorinator reactor at a temperature of 400°C to form 1,1,1-trichloroethane and hydrogen chloride. Crude trichloroethane, the hydrogen chloride produced, and excess dichloroethane are recycled to the hydrochlorinator reactor. Crude trichloroethane, obtained as the high boiling fraction from the purification column, is steam stripped and distilled to produce 1,1,1-trichloroethane for storage and sales.[13-15]

3. Oxyhydrochlorination

Oxyhydrochlorination entails the chlorination of a hydrocarbon with hydrogen chloride and oxygen (air). The products and processes used to manufacture chlorinated hydrocarbons pertinent to this study are summarized in Table 5 together with the chemical equation representing each reaction.

TABLE 5. OXYHYDROCHLORINATION PROCESSES

Product	Manufacturing process	Chemical reactions	Equation No.
Ethylene dichloride	Oxyhydrochlorination of ethylene	$2CH_2{=}CH_2 + O_2 + 4HCl \rightarrow 2ClCH_2CH_2Cl + 2H_2O$	39
Trichloroethylene	Oxyhydrochlorination of ethylene dichloride	$ClCH_2{-}CH_2Cl + O_2 + HCl \rightarrow C_2HCl_3 + 2H_2O$	40

As indicated in Table 5, a typical oxyhydrochlorination reaction can be represented by a general chemical equation, such as:

$$\text{hydrocarbon} + \text{oxygen (air)} + \begin{matrix}\text{hydrogen}\\ \text{chloride}\end{matrix} \rightarrow \begin{matrix}\text{chlorinated}\\ \text{hydrocarbon}\end{matrix} + \text{water} + \text{(byproducts)} \qquad (41)$$

The overall stoichiometric equation for oxyhydrochlorination processes is:

$$C_xH_yCl_zO_w + (K_1)HCl + (K_2)O_2 \rightarrow C_aH_bCl_d + (K_3)H_2O \qquad (42)$$

where $K_1 = d - z$

$$K_2 = \frac{d + y - z - b}{4} - \frac{w}{2}$$

$$K_3 = \frac{d + y - z - b}{2}$$

The oxyhydrochlorination process used in the manufacture of the above two chlorinated hydrocarbons consists of three basic steps: (1) oxyhydrochlorination, (2) absorption, and (3) separation. Oxyhydrochlorination reactions are usually exothermic. In the reactor, which must be designed for efficient heat removel, hydrocarbon, hydrogen chloride, and oxygen react to form the chlorinated hydrocarbon. The reaction is dependent on various factors, including hydrocarbon and catalyst used, reaction temperature and pressure, and the ratio of hydrogen chloride to hydrocarbon. The effluents from the reactor include crude product, byproducts, unreacted raw materials, and catalyst (when used).

Resulting reaction products are sent to an absorber where unreacted hydrogen chloride is removed and the reaction products are condensed. Remaining hydrogen chloride is removed by scrubbing with caustic. Crude product is then purified by separation. Separation can be carried out in a single unit or a series of multiple units and includes distillation, stripping, or phase separation. Pure product is separated from byproducts and is withdrawn and sent to storage.

a. Oxyhydrochlorination of Ethylene--
Ethylene dichloride is manufactured by oxyhydrochlorination of ethylene.

(1) Chemistry--The chemical reaction for the oxyhydrochlorination of ethylene to produce ethylene dichloride can be represented as follows:[13,15,21,30-32]

$$\underset{\text{(ethylene)}}{2CH_2{=}CH_2} + \underset{\text{(oxygen)}}{O_2} + \underset{\text{(hydrogen chloride)}}{4HCl} \rightarrow \underset{\text{(ethylene dichloride)}}{2ClCH_2CH_2Cl} + \underset{\text{(water)}}{2H_2O} \quad (43)$$

Air and hydrogen chloride react with ethylene in a fluidized- or fixed-bed catalytic process to produce ethylene dichloride. The catalyst used is a mixture of copper chloride and other chlorides. Reactor temperature varies between 180°C and 280°C,

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[30] DeForest, E. M., and S. E. Penner. Fired-Bed Oxychlorination Yields 1,2-Dichloroethane. Chemical Engineering, 79(17):54-55, 1972.

[31] Schwartz, W. A., F. B. Higgins, Jr., J. A. Lee, R. Newirth, and J. W. Pervier. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume 3: Ethylene Dichloride Manufacture by Oxychlorination. EPA-450/3-73-006-c (PB 240 492), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1974. 104 pp.

[32] Hahn, A. V. The Petrochemical Industry, Market and Economics. McGraw-Hill Book Company, New York, New York, 1970. 620 pp.

and pressure ranges from 340 to 680 kPa gage (50 to 100 psig). Yields are over 90% based on ethylene, depending on the presence of excess ethylene or hydrogen chloride. Excess hydrogen chloride favors the reaction.[13,15]

(2) Process--Figure 10 is a simple block flow diagram for the oxyhydrochlorination of ethylene to produce ethylene dichloride.[13,15,30,31] Stoichiometric amounts of ethylene, anhydrous hydrogen chloride, and air are fed to a catalytic reactor. The air is compressed and preheated prior to entering the reactor as a means of initiating the reaction. Conversion of ethylene is virtually complete in one flow through the reactor. The reaction is highly exothermic,, and heat is recovered, as steam, with internal cooling coils or fixed-bed multitube reactors, which resemble a heat exchanger, with the catalyst contained inside the tubes, while coolant flows through the shell.[31]

Effluent from the reactor is cooled by either direct water quench or indirect heat exchange. Condensed effluent is sent to a phase separator. Noncondensable gases consisting mainly of nitrogen are contacted in an absorber with either water or aromatic solvent for removal of HCl and recovery of ethylene dichloride before venting to the atmosphere.[15,31]

The organic liquid product obtained in the phase separator and from the ethylene dichloride stripper is contacted with aqueous caustic soda to neutralize any remaining hydrogen chloride. Effluent from the neutralizer is distilled for removal of water and chlorinated hydrocarbon impurities, which are recovered as overhead and sent to waste disposal.[15,31] Bottoms from the heads column, which consist mainly (96% to 98%) of ethylene dichloride, are sent to the final products finishing column. Pure ethylene dichloride is obtained as overhead and sent to storage. Bottoms consisting of heavy ends are sent to waste disposal.[31]

b. Oxyhydrochlorination of Ethylene Dichloride--Trichloroethylene is manufactured by oxyhydrochlorination of ethylene dichloride.

(1) Chemistry--The chemical reaction for the oxyhydrochlorination of ethylene dichloride to produce trichloroethylene can be represented as follows:[13,15,19]

$$\underset{\substack{\text{(oxygen)}\\ \text{(air)}}}{O_2} + \underset{\substack{\text{(hydrogen}\\ \text{chloride)}}}{HCl} + \underset{\substack{\text{(ethylene}\\ \text{dichloride)}}}{ClCH_2CH_2Cl} \rightarrow \underset{\text{(trichloroethylene)}}{C_2HCl_3} + \underset{\text{(water)}}{2H_2O} \tag{44}$$

Copper chloride is used as catalyst in a vapor phase reaction at 300°C to 400°C under 690 kPa gage (100 psig) pressure.[28]

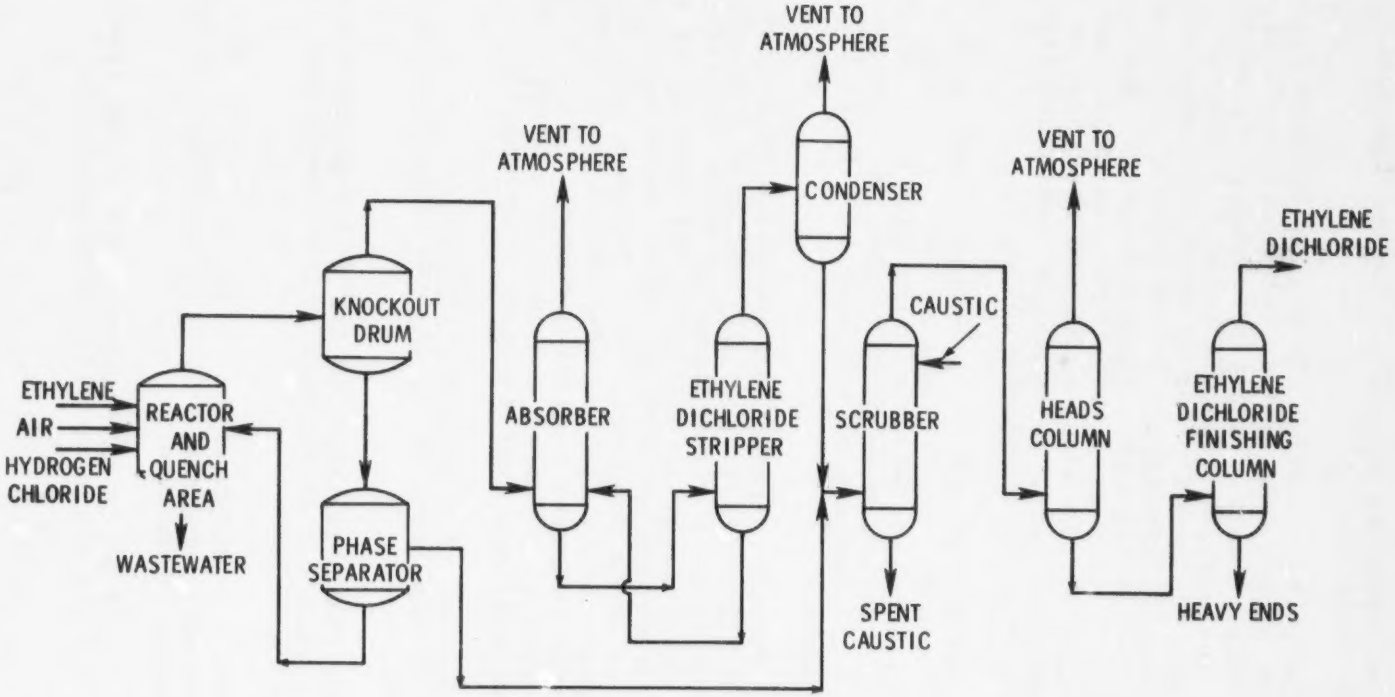
VENT TO ATMOSPHERE
VENT TO ATMOSPHERE
CONDENSER
VENT TO ATMOSPHERE
ETHYLENE DICHLORIDE
KNOCKOUT DRUM
CAUSTIC
ETHYLENE
AIR
HYDROGEN CHLORIDE
REACTOR AND QUENCH AREA
ABSORBER
ETHYLENE DICHLORIDE STRIPPER
SCRUBBER
HEADS COLUMN
ETHYLENE DICHLORIDE FINISHING COLUMN
WASTEWATER
PHASE SEPARATOR
SPENT CAUSTIC
HEAVY ENDS

Figure 10. Ethylene dichloride by the oxyhydrochlorination of ethylene.[13,15,30,31]

(2) Process--Figure 11 is a simple block flow diagram for the oxyhydrochlorination of ethylene dichloride to produce trichloroethylene.[13,15,33-37]

Air, ethylene dichloride, and an excess of hydrogen chloride (or chlorine) are mixed in a tubular reactor at 300°C to 400°C and ∿690 kPa gage. The reaction is highly exothermic and requires cooling of the reactor.[13,15,34-37]

Effluents from the reactor pass through an absorber where excess hydrogen chloride is absorbed. Absorbed products are condensed after caustic scrubbing. The noncondensables are recycled to the absorber and, if still not condensed, vented to the atmosphere. Crude product from the phase separator is fed to the stripper, where the heavy ends are separated from the crude trichloroethylene. Effluent from the stripper is fed to a product purification column where light ends are fractionated from the pure product. Trichloroethylene is obtained as bottoms and fed to product storage.[13,15,19,33,34,38]

4. Chlorohydrination

Chlorohydrination reactions consist of chlorination of a hydrocarbon with hypochlorous acid. The products and processes used to manufacture chlorinated hydrocarbons pertinent to this study are summarized in Table 6 together with the chemical equation representing each reaction.

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[33] Improvements in or relating to Perchloroethylene and Hydrogen Chloride Manufacture. British Patent 856,664 (to Diamond Alkali Company), December 21, 1960. 7 pp.

[34] PPG Industries: Chlorinated Solvents from Ethylene. Chemical Engineering, 76(26):90-91, 1969.

[35] Perchlor and trichlor (per/tri) - PPG Industries. Hydrocarbon Processing, 52(11):157, 1973.

[36] Kroop, J. F., and G. R. Neikirk. Oxychlorinate for per/tri. Hydrocarbon Processing, 51(11):109-110, 1972.

[37] Perchloroethylene-trichloroethylene - PPG Industries, Inc. Hydrocarbon Processing, 54(11):169, 1975.

[38] Production of Chlorinated Hydrocarbons. British Patent 913,040 (to Pittsburgh Plate Glass Company), December 12, 1962. 9 pp.

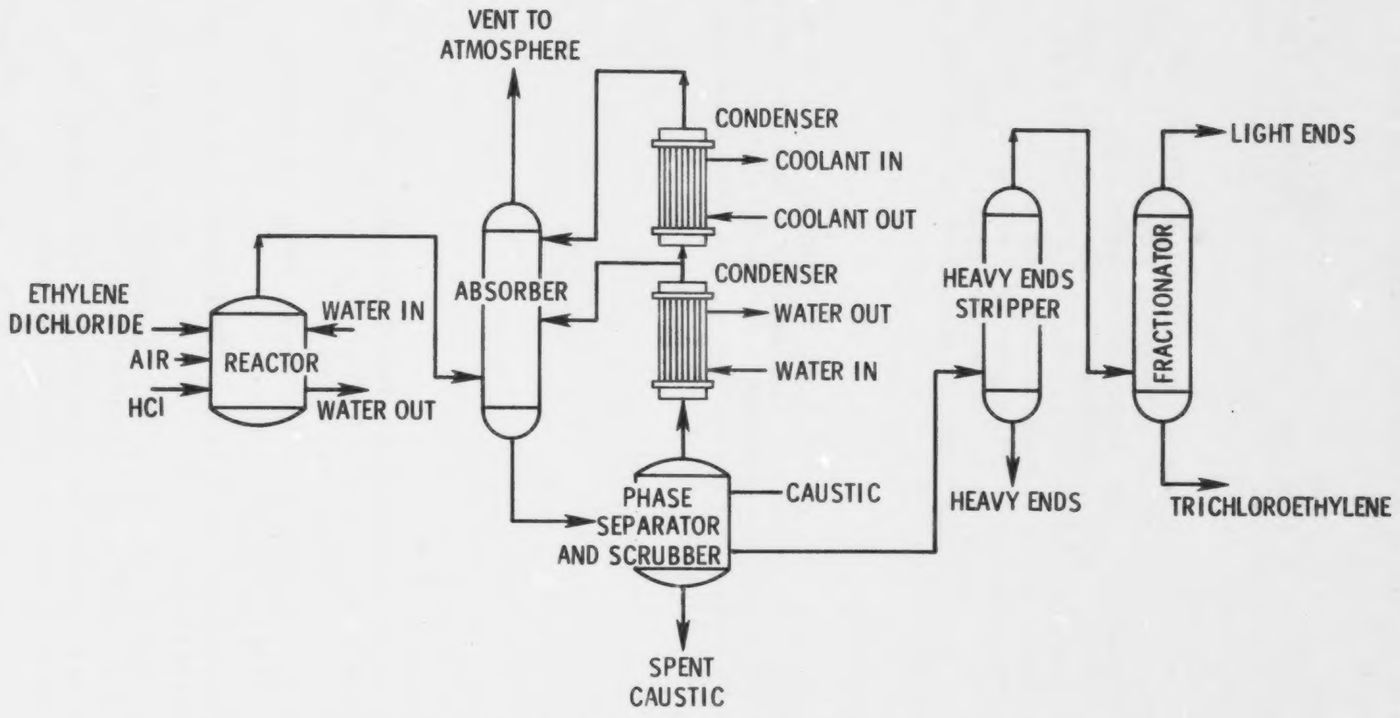
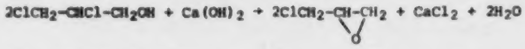
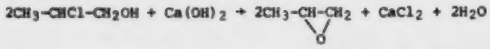

VENT TO ATMOSPHERE
ETHYLENE DICHLORIDE
AIR
HCl
REACTOR
WATER IN
WATER OUT
ABSORBER
CONDENSER
COOLANT IN
COOLANT OUT
CONDENSER
WATER OUT
WATER IN
PHASE SEPARATOR AND SCRUBBER
CAUSTIC
SPENT CAUSTIC
HEAVY ENDS STRIPPER
HEAVY ENDS
FRACTIONATOR
LIGHT ENDS
TRICHLOROETHYLENE

Figure 11. Trichloroethylene by the oxyhydrochlorination of ethylene dichloride.[13,15,33-37]

TABLE 6. CHLOROHYDRINATION PROCESSES

Product	Manufacturing process	Chemical reactions	Equation No.
Epichlorohydrin	Chlorohydrination of allyl chloride	$Cl_2 + H_2O \rightleftarrows HCl + HOCl$	45
		$ClCH_2\text{-}CH{=}CH_2 + HOCl \rightarrow ClCH_2\text{-}CHCl\text{-}CH_2OH$	46
		 $2ClCH_2\text{-}CHCl\text{-}CH_2OH + Ca(OH)_2 \rightarrow 2ClCH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + CaCl_2 + 2H_2O$	47
Propylene oxide	Chlorohydrination of propylene	$Cl_2 + H_2O \rightleftarrows HCl + HOCl$	48
		$CH_3\text{-}CH{=}CH_2 + HOCl \rightarrow CH_3\text{-}CHCl\text{-}CH_2OH$	49
		 $2CH_3\text{-}CHCl\text{-}CH_2OH + Ca(OH)_2 \rightarrow 2CH_3\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + CaCl_2 + 2H_2O$	50

A typical chlorohydrination reaction can be represented by a general chemical equation such as:

Hydrocarbon + chlorine + water + calcium hydroxide →
hydrogen chloride + water + calcium chloride + chlorinated hydrocarbon (51)

The overall stoichiometric equation describing chlorohydrination processes is:

$$C_wH_xCl_y + (K_1)HOCl + (K_2)Ca(OH) \rightarrow C_aH_bCl_dO_e + (K_3)H_2O + (K_4)CaCl_2 \quad (52)$$

where $K_1 = \frac{2}{3}(2e + x - b + \frac{d}{2} - \frac{y}{2})$

$$K_2 = K_4 = \frac{1}{3}(2e + x - b - d + y)$$

$$K_3 = e + x - b$$

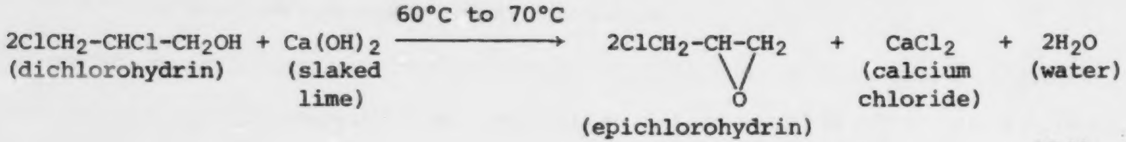
The chlorohydrination process used in the manufacture of the above two chlorinated hydrocarbons consists of five basic steps: (1) acid generation, (2) chlorohydrination, (3) separation, (4) conversion, and (5) separation.

Hypochlorous acid is generated by dissolving chlorine in water in a packed tower. The hydrocarbon is chlorohydrinated with hypochlorous acid in a stirred tank reactor. Reactor effluents are separated by phase separation into unreacted hypochlorous acid, which is recycled back to the packed tower, and chlorohydrin. Chlorohydrin is fed to the second reactor where it is converted by reaction with lime slurry to the required product. Effluent from the converter (second reactor) is separated into crude product and byproducts. The crude product is further fractionated to recover pure product and byproducts.

a. Chlorohydrination of Allyl Chloride--
Epichlorohydrin is produced by chlorohydrination of allyl chloride.

(1) Chemistry--The chemical reactions for the chlorohydrination of allyl chloride to produce epichlorohydrin can be represented as follows:[13]

$$\underset{\text{(allyl chloride)}}{ClCH_2CH{=}CH_2} + \underset{\text{(hypochlorous acid)}}{HOCl} \xrightarrow{30°C \text{ to } 40°C} \underset{\text{(dichlorohydrin)}}{ClCH_2\text{-}CHCl\text{-}CH_2OH} \qquad (53)$$



$$\underset{\text{(dichlorohydrin)}}{2ClCH_2\text{-}CHCl\text{-}CH_2OH} + \underset{\text{(slaked lime)}}{Ca(OH)_2} \xrightarrow{60°C \text{ to } 70°C} \underset{\text{(epichlorohydrin)}}{2ClCH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2}} + \underset{\text{(calcium chloride)}}{CaCl_2} + \underset{\text{(water)}}{2H_2O}$$

(54)

(2) Process--Figure 12 is a simple block flow diagram for the production of epichlorohydrin by chlorohydrination of allyl chloride.[13]

Allyl chloride is fed continuously to a stirred tank where it reacts at atmospheric pressure and at 30°C to 40°C in the liquid phase with a solution of hypochlorous acid.[14] Hypochlorous acid is produced in a packed tower by dissolving chlorine in water. Reaction tank effluent is fed to a separator, and the upper layer (aqueous phase) is recycled to the hypochlorous acid tower.[14] The bottoms, chiefly dichlorohydrins, are fed to the second agitated reactor, where virtually quantitative conversion to epichlorohydrin occurs by reaction with lime slurry. Trichloropropane is used as a solvent for the epichlorohydrin.[14] Effluent from the second reactor is steam stripped, removing epichlorohydrin as the water azeotrope. The bottoms, calcium chloride solution, and excess lime in suspension are sent to byproduct recovery or discharged to the water treatment facility. The water and organic phases in the distillate are separated, and the bottoms are fed to a fractionating tower for recovery of epichlorohydrin and solvent. Purified epichlorohydrin is sent to storage. Recovered solvent is recycled.[13,14]

b. Chlorohydrination of Propylene--
Propylene oxide is manufactured by chlorohydrination of propylene.

(1) Chemistry--The chemical reactions for the chlorohydrination of propylene to produce propylene oxide can be represented as follows:[13,15,25,39-42]

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[39] Fyvie, A. C. Propylene Oxide and Its Derivatives. Chemistry and Industry, 83(10):384-388, 1964.

[40] Stobaugh, R. B., V. A. Calarco, R. A. Morris, and L. W. Stroud. Propylene Oxide: How, Where, Who - Future. Hydrocarbon Processing, 52(1):99-108, 1973.

(continued)

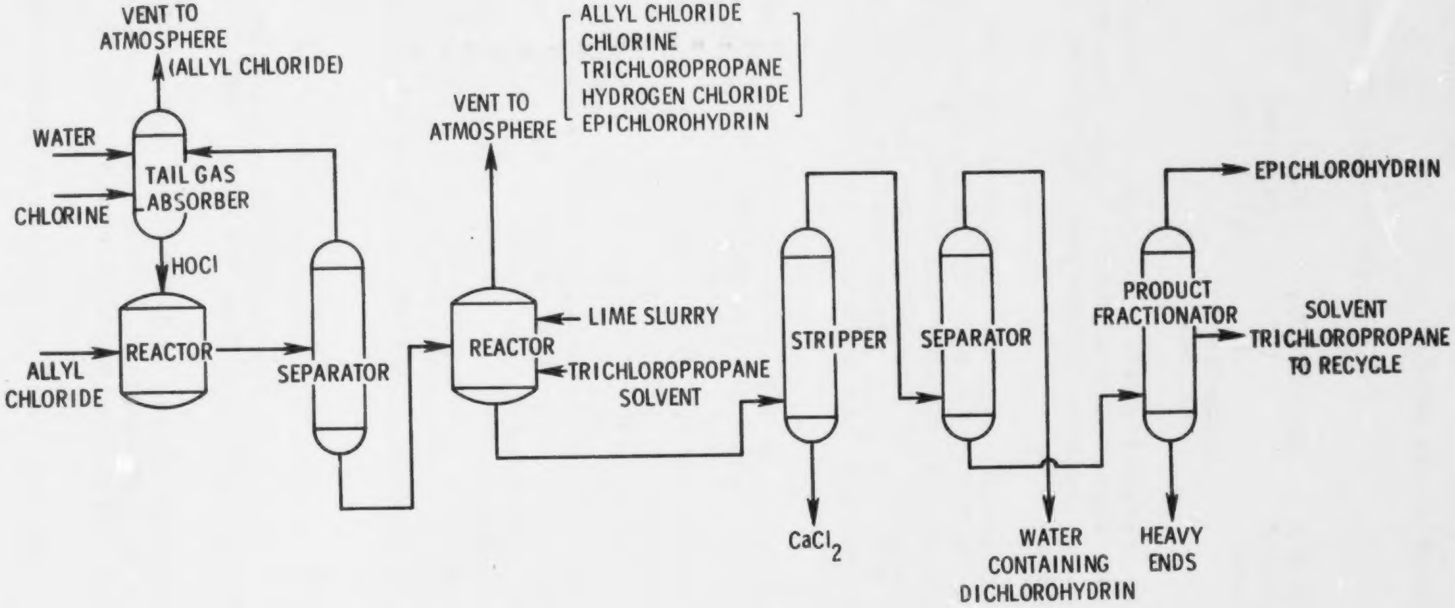
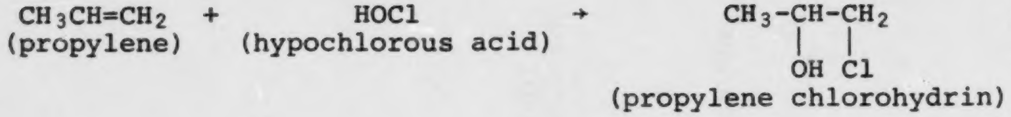
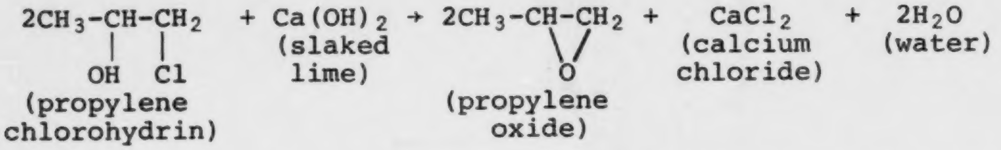

VENT TO ATMOSPHERE (ALLYL CHLORIDE)
WATER
CHLORINE
TAIL GAS ABSORBER
HOCl
ALLYL CHLORIDE
REACTOR
SEPARATOR
VENT TO ATMOSPHERE
ALLYL CHLORIDE
CHLORINE
TRICHLOROPROPANE
HYDROGEN CHLORIDE
EPICHLOROHYDRIN
REACTOR
LIME SLURRY
TRICHLOROPROPANE SOLVENT
STRIPPER
CaCl2
SEPARATOR
WATER CONTAINING DICHLOROHYDRIN
PRODUCT FRACTIONATOR
EPICHLOROHYDRIN
SOLVENT TRICHLOROPROPANE TO RECYCLE
HEAVY ENDS

Figure 12. Epichlorohydrin by the chlorohydrination of allyl chloride.[13,14]



$$\underset{\text{(propylene)}}{CH_3CH{=}CH_2} + \underset{\text{(hypochlorous acid)}}{HOCl} \rightarrow \underset{\text{(propylene chlorohydrin)}}{\underset{OH\quad Cl}{CH_3\text{-}CH\text{-}CH_2}} \qquad (55)$$



$$\underset{\text{(propylene chlorohydrin)}}{2\underset{OH\quad Cl}{CH_3\text{-}CH\text{-}CH_2}} + \underset{\text{(slaked lime)}}{Ca(OH)_2} \rightarrow \underset{\text{(propylene oxide)}}{2\underset{O}{CH_3\text{-}CH\text{-}CH_2}} + \underset{\text{(calcium chloride)}}{CaCl_2} + \underset{\text{(water)}}{2H_2O} \qquad (56)$$

In aqueous solution, several reactions occur in addition to the chlorohydrination reaction. Byproducts include isomers of propylene chlorohydrin, propylene dichloride, dichlorodiisopropyl ether, and chloroacetone.[39]

The saponification reaction must be completed rapidly since propylene chlorohydrin is volatile and, if unconverted, may be lost in the aqueous effluent. Propylene oxide formed in the above manner is rapidly hydrated to monopropylene glycol by the alkaline conditions in the reactor. Therefore, it is important that the oxide be recovered from the solution as quickly as possible after it is formed.[39]

(2) Process--Figure 13 is a simple block flow diagram for the production of propylene oxide by the chlorohydrination of propylene.[13,15,39,40,43] Propylene, chlorine, and water are introduced into a reactor where they react under controlled conditions to form propylene chlorohydrin. Actually, the chlorine and water react to form hypochlorous acid (HOCl) and hydrochloric acid (HCl) which, under the conditions in the tower, react much more rapidly with the propylene present than the chlorine does. The chlorine/propylene ratio of the gaseous feed to the tower is so chosen that the liquid effluent leaving the tower contains 3% to 4% propylene chlorohydrin.[13] It is necessary to operate in dilute solution to avoid a separate propylene chloride oil phase which would preferentially dissolve chlorine and propylene with increased conversion to the undesirable byproduct propylene

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(continued)

[41] Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 16. John Wiley & Sons, Inc., New York, New York, 1968. pp. 595-609.

[42] Lunde, K. E. Propylene Oxide and Ethylene Oxide. Report No. 2 (a private report by the Process Economics Program), Stanford Research Institute, Menlo Park, California, January 1965. 311 pp.

[43] Propylene Oxide - Caicel Ltd. Hydrocarbon Processing, 54(11):202, 1975.

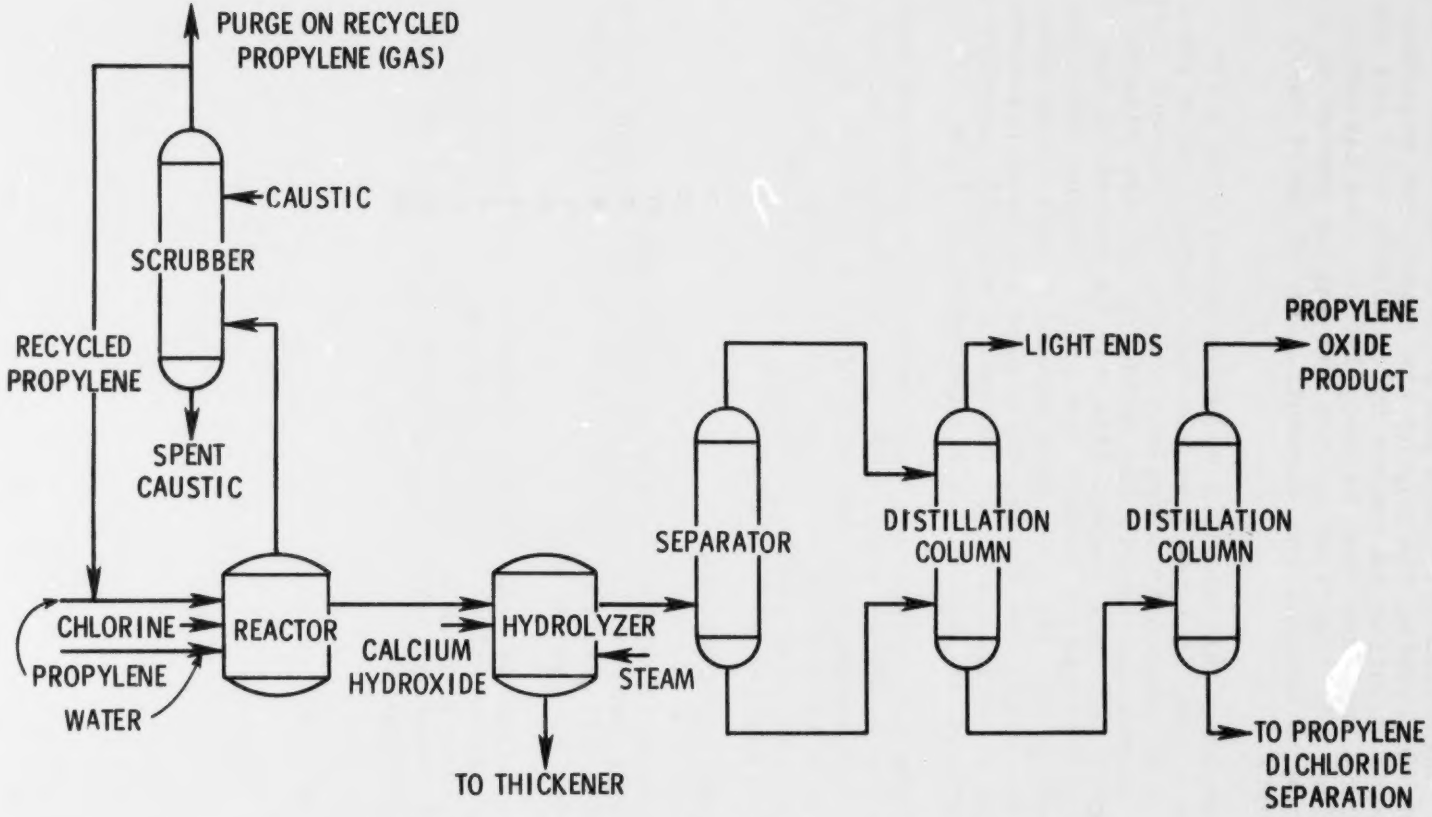
PURGE ON RECYCLED PROPYLENE (GAS)
CAUSTIC
SCRUBBER
RECYCLED PROPYLENE
SPENT CAUSTIC
CHLORINE
PROPYLENE
WATER
REACTOR
CALCIUM HYDROXIDE
HYDROLYZER
STEAM
TO THICKENER
SEPARATOR
DISTILLATION COLUMN
LIGHT ENDS
DISTILLATION COLUMN
PROPYLENE OXIDE PRODUCT
TO PROPYLENE DICHLORIDE SEPARATION

Figure 13. Propylene oxide by the chlorohydrination of propylene.[13,15,39,40,43]

dichloride.[13] Unreacted propylene and propane contained in the propylene feed, on leaving the top of the tower, are scrubbed with caustic soda solution to remove hydrochloric acid and any residual chlorine, and may then be recycled or used elsewhere in the plant as fuel.[13] A portion of the gas may be vented to fuel or incinceration to control the concentration of inert gases in a recycle process.

The dilute propylene chlorohydrin solution mixed with a 10% slurry of slaked lime is pumped to the hydrolyser. Here the chlorohydrin is converted to propylene oxide. To prevent further hydrolysis to propylene glycol, the oxide is rapidly flashed out of the reaction zone. The excess lime may be recovered for recycle in thickeners which remove the spent calcium chloride brine by decantation. The lime used should contain less than 1% magnesium oxide, since the latter catalyses the isomerization of propylene oxide to aldehydes. If economics warrant, caustic soda may be used instead of lime or as a supplement to lime.[13]

The overhead from the hydrolyser, predominantly propylene oxide and water, is contaminated with propylene dichloride, chloropropenes from dehydrohalogenation of propylene chloride and propionaldehyde from isomerization of propylene oxide. The oxide is purified by fractionation in multiple distillation columns to produce a specification grade product.[13]

B. GEOGRAPHICAL DISTRIBUTION

In 1975 there were 32 companies with a total capacity of 11.5×10^6 metric tons/yr at 58 locations in the United States producing 8.52×10^6 metric tons of the 14 chlorinated hydrocarbons included in this study.

Most of the chlorinated hydrocarbon industry, as shown in Figure 14, is concentrated in three regions: Northeastern, South Central, and the West. Table 7[1-12] lists manufacturing company, plant location, capacity, product type, and population density of each region.

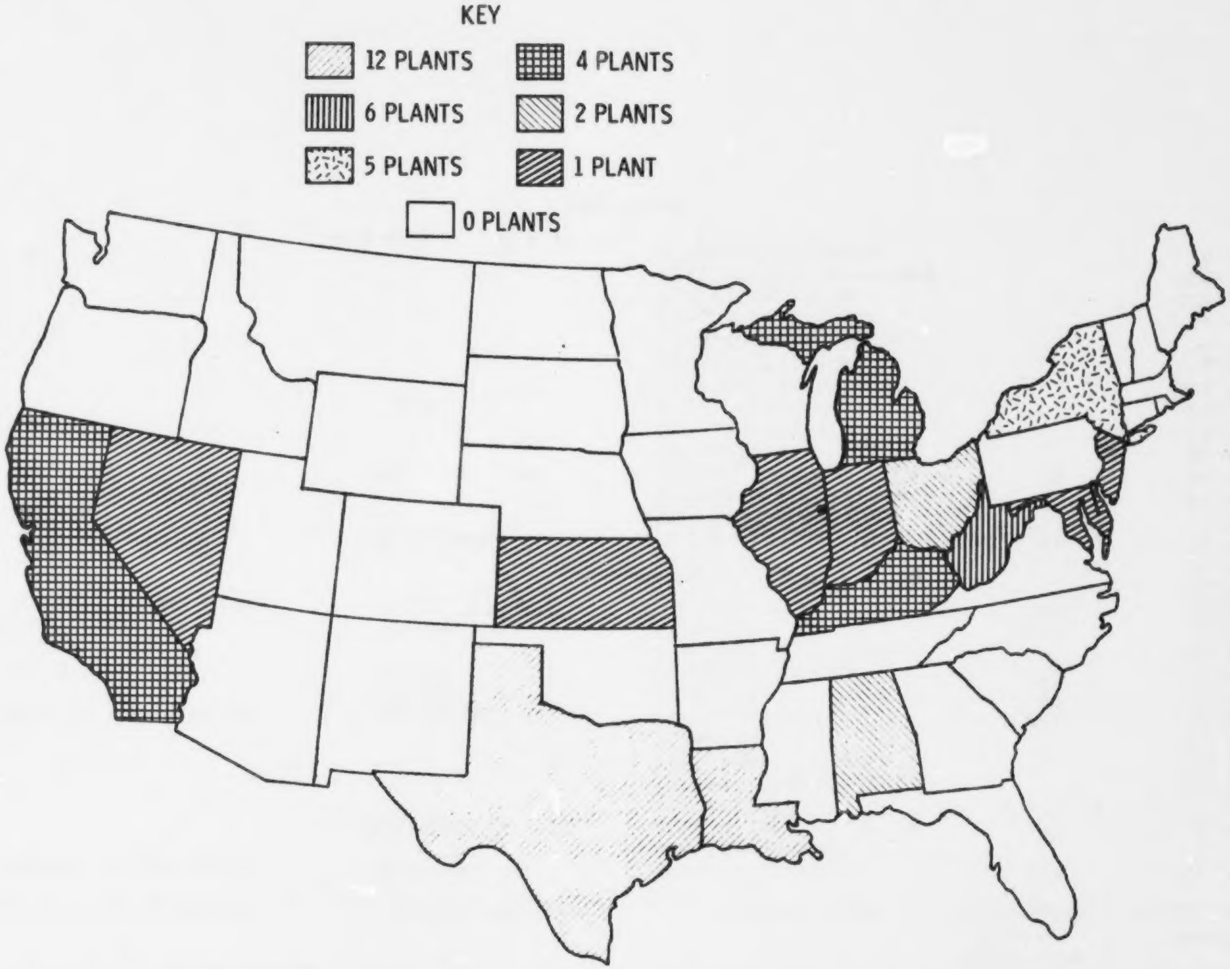
KEY
12 PLANTS
4 PLANTS
6 PLANTS
2 PLANTS
5 PLANTS
1 PLANT
0 PLANTS

Figure 14. Geographical distribution of chlorinated hydrocarbon plants.

TABLE 7. CHLORINATED HYDROCARBON MANUFACTURING FACILITIES INCLUDING COMPANY, PLANT LOCATIONS, PRODUCT TYPES, POPULATION DENSITY, AND CAPACITY.[1-12]

Manufacturing company	Plant location	Product type	Population density, persons/km^2	Capacity, metric tons/yr
Allied Chemical Corporation	Syracuse, NY	Monochlorobenzene	222	11,300
		Dichlorobenzene		7,300
	Moundsville, WV	Carbon tetrachloride	47	3,600
		Chloroform		13,600
		Methyl chloride		11,300
		Methylene chloride		22,700
		Phosgene		44,500
BASF, Wyandotte Corporation	Wyandotte, MI	Propylene oxide	1,686	79,400
	Geismar, LA	Phosgene	47	24,900
Continental Oil Company	Lake Charles LA	Methyl chloride	50	45,400
		Ethylene dichloride		535,900
Chemetron Corporation	LaPorte, TX	Phosgene	386	9,100
Diamond Shamrock Corporation	Belle, WV	Chloroform	95	18,100
		Methyl chloride		11,300
		Methylene chloride		45,400
	Deer Park, TX	Perchloroethylene	386	74,800
		Trichloroethylene		22,700
		Ethylene dichloride		199,600
Dow Chemical, U.S.A.	Freeport, TX	Carbon tetrachloride	29	61,200
		Chloroform		45,400
		Epichlorohydrin		113,400
		Ethyl chloride		34,000
		Ethylene dichloride		725,700
		Methyl chloride		31,800
		Methylene chloride		90,700
		Perchloroethylene		54,400
		Propylene oxide		415,000
		1,1,1-Trichloroethane		204,100
		Trichloroethylene		68,000

(continued)

TABLE 7 (continued)

Manufacturing company	Plant location	Product type	Population density, persons/km^2	Capacity, metric tons/yr
Dow Chemical, U.S.A. (continued)	Midland, MI	Monochlorobenzene	47	136,100
		Dichlorobenzene		27,200
	Oyster Creek, TX	Ethylene dichloride	386	499,000
	Pittsburg, CA	Perchloroethylene	290	9,100
		Carbon tetrachloride		36,300
	Plaquemine, LA	Carbon tetrachloride	19	56,700
		Chloroform		45,300
		Ethylene dichloride		601,000
		Methyl chloride		68,000
		Methylene chloride		81,600
		Perchloroethylene		68,000
		Propylene oxide		154,200
Dow Corning Corporation	Carrollton, KY	Methyl chloride	25	9,100
	Midland, MI	Methyl chloride	47	6,800
E.I. duPont De Nemours & Co., Inc.	Corpus Christi, TX	Carbon tetrachloride	27	136,100
	Deepwater Point, NJ	Ethyl chloride	64	49,900
		Phosgene		61,200
Ethyl Corporation	Baton Rouge, LA	Ethyl chloride	233	95,300
		Ethylene dichloride		317,500
		Methyl chloride		45,400
		Perchloroethylene		45,400
		1,1,1-Trichloroethane		22,700
		Trichloroethylene		18,100
	Houston, TX	Ethylene dichloride	386	118,000
		Ethyl chloride		68,000
F.M.C. Corporation	S. Charleston, WV	Carbon tetrachloride	95	136,100
	Baltimore, MD	Phosgene	493	2,700
General Electric	Mount Vernon, IN	Phosgene	20	27,200
	Waterford, NY	Methyl chloride	57	22,700

(continued)

TABLE 7 (continued)

Manufacturing company	Plant location	Product type	Population density, persons/km^2	Capacity, metric tons/yr
The B. F. Goodrich Company	Calvert City, KY	Ethylene dichloride	25	453,600
Hooker Chemical Corporation	Taft, LA	Perchloroethylene	37	27,200
		Trichloroethylene		18,100
Jefferson Chemical Company	Port Neches, TX	Phosgene	98	13,600
		Propylene oxide		68,000
Mobay Chemical Corporation	New Martinsville, WV	Phosgene	21	111,100
	Cedar Bayou, TX	Phosgene	98	59,000
Monsanto Company	Sauget, IL	Monochlorobenzene	161	52,200
		Dichlorobenzene		12,700
Montrose Chemical Corporation	Henderson, NV	Monochlorobenzene	13	31,800
Olin Corporation	Ashtabula, OH	Phosgene	53	22,700
	Lake Charles, LA	Phosgene	50	54,400
	Brandenburg, KY	Propylene oxide	23	59,000
Oxirane Corporation	Bayport, TX	Propylene oxide	386	417,300
PPG Industries, Inc.	Barberton, OH	Phosgene	514	2,300
	Lake Charles, LA	Ethyl chloride	50	54,400
		Ethylene dichloride		544,300
		Perchloroethylene		108,900
		1,1,1-Trichloroethane		79,400
		Trichloroethylene		90,700
	Natrium, WV	Dichlorobenzene	88	18,600
		Monochlorobenzene		31,800
Rubicon Corporation	Geismar, LA	Phosgene	47	56,700
Shell Chemical Company	Deer Park, TX	Ethylene dichloride	386	544,300
		Ethyl chloride		38,600
		Epichlorohydrin		63,500
	Norco, LA	Epichlorohydrin	37	27,200
		Ethylene dichloride		528,400

(continued)

TABLE 7 (continued)

Manufacturing company	Plant location	Product type	Population density, persons/km^2	Capacity, metric tons/yr
Solvent Chemical Company	Niagara Falls, NY	Dichlorobenzene	169	9,100
Specialty Organics, Inc.	Irwindale, CA	Dichlorobenzene	662	1,800
Standard Chlorine Chem. Co., Inc.	Delaware City, DE	Dichlorobenzene	341	56,700
		Monochlorobenzene		34,000
Stauffer Chemical Company	Carson, CA	Ethyl chloride	662	45,400
	Cold Creek, AL	Phosgene	6	11,300
	Le Moyne, AL	Carbon tetrachloride	6	90,700
	Carson, CA	Ethylene dichloride	662	154,200
	Louisville, KY	Carbon tetrachloride	709	15,900
		Chloroform		34,000
		Methyl chloride		6,800
		Methylene chloride		27,200
	Niagara Falls, NY	Carbon tetrachloride	169	68,000
Story Chemical Corporation	Muskegon, MI	Phosgene	120	4,500
Union Carbide Corporation	Institute, WV	Phosgene	95	49,900
		Methyl chloride		22,700
	Taft, LA	Ethylene dichloride	37	68,000
	Texas City, TX	Ethylene dichloride	160	68,000
The Upjohn Company	LaPort, TX	Phosgene	386	90,700
Van De Mark Chemical Compant, Inc.	Lockport, NY	Phosgene	169	3,600
Vulcan Materials Company	Geismar, LA	Carbon tetrachloride	47	40,800
		Chloroform		80,900
		Ethylene dichloride		149,700
		Methylene chloride		36,300
		Perchloroethylene		68,000
		1,1,1-Trichloroethane		29,500
	Wichita, KS	Carbon tetrachloride	134	27,200
		Chloroform		18,100
		Methylene chloride		13,600
		Perchloroethylene		22,700

SECTION IV

EMISSIONS

A. SELECTED POLLUTANTS

Process emissions from the chlorinated hydrocarbon industry are usually hydrocarbons. These may be raw materials, impurities in the raw materials, products, and byproducts. Major sources of hydrocarbon emissions to the atmosphere within the chlorinated hydrocarbon industry include emissions from the main process vent and from the product fractionation vent, storage tank emissions, fugitive emissions, and emissions from waste disposal. Due to the complexity of this industry in terms of the wide range of products and byproducts, plant sizes, and operating rates, and a lack of data on the entire industry, storage tank emissions, fugitive emissions, and emissions from waste disposal will be discussed but not evaluated. Table 8 summarizes the unit operations involved in the manufacture of each chlorinated hydrocarbon and identifies emission points.

On the basis of data available in the literature, the materials listed in Table 9 were identified as being emitted during the manufacture of chlorinated hydrocarbons and were selected for detailed analysis in this study. Also listed in Table 9 are the threshold limit values (TLV's) for each compound.[44]

B. LOCATIONS AND DESCRIPTIONS

1. Emissions from Main Process Vent

Atmospheric emissions from the main process vent, usually vented from an absorber or a scrubber, generally consist of chlorine, hydrogen chloride, and process raw materials, products, and byproducts. They represent a small percentage of the gross reactor effluents that are not recovered in the absorber or scrubber system. This source of emission is usually the primary one within a chlorinated hydrocarbon manufacturing facility. The composition of these emissions varies within the industry, based on the chlorinated hydrocarbon being manufactured. Within a

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[44] TLV's®. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1975. 97 pp.

TABLE 8. UNIT OPERATIONS INVOLVED IN THE MANUFACTURE OF CHLORINATED HYDROCARBONS WITH EMISSION SOURCES IDENTIFIED

		Unit operation[a]								
Product	Manufacturing process	Absorption	Drying	Fluid flow	Heat transfer	Material handling	Mixing	Separation	Storage	Waste disposal
Methyl chloride	**Direct chlorination of methane**	A	W	D	D	D	D	W	A	W
Methylene chloride	**Direct chlorination of methane**	A	W	D	D	D	D	W	A	W
Chloroform	Direct chlorination of methane	A	W	D	D	D	D	W	A	W
Carbon tetrachloride	Direct chlorination of methane	A	W	D	D	D	D	W	A	W
Carbon tetrachloride	Direct chlorination of carbon disulfide	A	-	D	-	D	D	A W S	A	W S
Carbon tetrachloride	Direct chlorination of propane	D	A W	D	D	D	D	W S	A	W S
Perchloroethylene	Direct chlorination of propane	D	A W	D	D	D	D	W S	A	W S
Ethylene dichloride	**Direct chlorination of ethylene**	A	-	D	D	D	D	W S	A	W S
Phosgene	Direct chlorination of carbon monoxide	A	-	D	D	D	-	-	A	A
Monochlorobenzene	Direct chlorination of benzene	A	-	D	D	D	-	W S	A	W S
Dichlorobenzene	Direct chlorination of benzene	A	-	D	D	D	-	W S	A	W S
Methyl chloride	Hydrochlorination of methanol	W	W	D	D	D	-	W S	A	W S
Ethyl chloride	Hydrochlorination of ethylene	-	-	D	-	D	D	A W	A	W
1,1,1-Trichloroethane	Hydrochlorination of vinyl chloride	-	-	D	A	D	-	A W	A	W
Ethylene dichloride	Oxyhydrochlorination of ethylene	A	-	D	D	D	-	A W S	A	W S
Trichloroethylene	Oxyhydrochlorination of ethylene dichloride	A	-	D	D	D	D	W S	A	W S
Epichlorohydrin	Chlorohydrination of allyl chloride	A	-	D	-	D	-	A W S	A	W S
Propylene oxide	Chlorohydrination of propylene	A W	-	D	-	D	-	W S	A	W S

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[a] A = Atmospheric emission, W = Wastewater discharge, S = Solid waste, D = Unit operation performed but no process emissions are anticipated, - = Unit operation not performed.

TABLE 9. MATERIAL EMITTED FROM CHLORINATED HYDROCARBON MANUFACTURING PLANTS

Material emitted	TLV, g/m³	Material emitted	TLV, g/m³
Allyl chloride	0.003	Ethylene dichloride	0.20
Epichlorohydrin	0.019	Hydrogen chloride	0.007
Vinyl chloride	0.0026	Vinylidene chloride	0.004
Propylene oxide	0.240	Phosgene	0.0002
Methane	0.710	Carbon monoxide	0.055
Butane	2.59	Toluene	0.375
Methyl chloride	0.210	Monochlorobenzene	0.35
Propylene	1.88	Dichlorobenzene	0.30
Methylene chloride	0.720	Ethane	1.34
Chloroform	0.120	Ethyl chloride	2.60
Carbon tetrachloride	0.065	Dichloroethane	0.82
Carbon disulfide	0.060	Trichloroethylene	0.535
Chlorine	0.003	Perchloroethylene	0.670
Sulfur monochloride	0.006	Trichloroethane	1.90
Ethylene	1.25	Trichloropropane	0.30
Dichloropropional		Benzene	0.0035
Bis(β-chloroisopropyl) ether	0.001	Dichloropropane	0.35
		Naphthalene	0.050
		Dichloroethylene	0.790

specific plant, these emissions depend on catalyst activity, reactor operating conditions, and the specific processing scheme employed.

2. Emissions from Product Fractionation Vent

The product fractionation vent represents a second major source of atmospheric emissions within the chlorinated hydrocarbon manufacturing industry. Stream composition varies greatly with the chlorinated hydrocarbon being manufactured, with the type of fractionation system used for product recovery, and with the desired product purity.

3. Emissions from Storage Tanks

Hydrocarbon vapors are emitted from storage tanks due to the volatility of the stored material. Heat or pressure changes within the tank affect the rate of evaporation of the stored material. Heat from direct solar radiation or from contact with warm ambient air, or heat introduced during processing can all be prime factors causing vaporization of the volatile stored material. The evaporation rate depends upon the atmospheric temperature, weather conditions, tank shell temperature, vapor space temperature, and liquid body and surface temperatures.[45]

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[45] Air Pollution Engineering Manual, Second Edition, J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

To a degree that depends upon the total vapor pressure exerted by the liquid at storage temperatures, the air in the vapor space of a storage tank will be saturated with vapor. As temperature and, correspondingly, pressure increase, some of this air vapor mixture will be emitted to the atmosphere.45

With temperature decrease occurring at night or resulting from cloudiness or rain, the vapor contracts, and fresh air is sucked into the storage tank, upsetting the existing equilibrium of saturation. More volatile hydrocarbons evaporate from the stored liquid in the tank to restore equilibrium. When the atmospheric temperature increases, as occurs with daylight, expansion occurs again and hydrocarbons are emitted. This cycle is repeated continually.45

Emissions from storage tanks also occur due to filling, with the rate of emission being proportional to the tank filling rate. Withdrawing liquid from storage tanks creates empty space, causing fresh air to enter the tank and allowing more evaporation to occur.45

Wind blowing through a free-vented tank also causes an emission problem, termed windage emissions. The quantity of emission from this source is not as large as that from breathing or filling cycles.45

Emission problems associated with floating roof tanks are different and are known as wicking and wetting. Wicking emissions are caused by the capillary flow of the liquid between the outer side of the sealing ring and the inner side of the tank wall. Wetting emissions occur when the floating roof moves toward the bottom of the tank during emptying and leaves the inner tank shell covered with a film of liquid, which evaporates when exposed to the atmosphere.45

4. Fugitive Emissions

Emissions occurring from pressure relief valves, pumps, compressors, agitator seals, valve stems, and flanges; from process upsets; and from loading and unloading of raw materials, products, and byproducts; purging of equipment before reports; and sampling for laboratory analysis are defined as fugitive emissions.

Due to the complexity of the chlorinated hydrocarbon manufacturing industry in terms of the different products manufactured, the large range of plant sizes, and the lack of data on fugitive emissions, the emissions from this source will not be determined.

5. Emissions from Waste Disposal

Liquid and solid wastes are generated during the manufacture of chlorinated hydrocarbons. When hydrogen chloride or chlorine reacts with hydrocarbons under various conditions, chlorinated hydrocarbons are formed. Along with the major product several byproducts are produced due to side reactions occuring with chlorine, hydrogen chloride, raw material, and contaminants present in the raw material. These byproducts will be present in liquid and solid waste streams.

Other sources of liquid waste include water condensed from the reactor effluent, plus spent caustic from the neutralizer and spent sulfuric acid from the dryer. The combined flow of streams varies considerably from plant to plant. The wastewater is usually sent for treatment or used for pH control in other processing areas. Other solid waste, consisting primarily of catalyst particles removed from the reactor effluent, may be removed from the reject water settling ponds. Since this report deals with atmospheric pollution, the quantities of liquid and solid waste generated will not be studied in this report.

C. EMISSION FACTORS

Tables 10 through 13 list products, manufacturing processes, unit operations, materials emitted, and emission factors for all chlorinated hydrocarbons being studied for this project and manufactured by the four process types (direct chlorination, hydrochlorination, oxyhydrochlorination, and chlorohydrination).

The emission factors were derived from field sampling, and emission data and material balances reported in References 14, 15, 20, 31, and 42, and the following personal communications:

- T. H. Capps, Allied Chemical Company, Moundsville, West Virginia, July 28, 1976.
- J. R. Hofts, FMC Corporation, South Charleston, West Virginia, November 10, 1976.
- R. A. Coates, Mobay Chemical Company, New Martinsville, West Virginia, April 1, 1976.

Total hydrocarbon values reported in Tables 10 - 13 include all compounds containing a hydrogen-carbon bond. The value is reported in methane equivalents and cannot therefore be obtained as a direct sum of the individual components.

TABLE 10. EMISSION FACTORS BY UNIT OPERATIONS FOR PROCESSES INVOLVING DIRECT CHLORINATION

Product	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg
Methyl chloride, methylene chloride, chloroform, and carbon tetrachloride	Direct chlorination of methane	Absorption	Total hydrocarbons (CH_4 equivalent)	0.012[a]
Carbon tetrachloride	Direct chlorination of carbon disulfide	Absorption	Carbon tetrachloride	2.57[b]
			Total hydrocarbons (CH_4 equivalent)	-[c]
		Separation	Carbon disulfide	2.00[d]
			Carbon tetrachloride	0.25[b]
			Chlorine	0.00015[d]
			Sulfur monochloride	1.00[d]
			Total hydrocarbons (CH_4 equivalent)	-[c]
Carbon tetrachloride and perchloroethylene	Direct chlorination of propane	Drying	Chlorine	10.00[d]
			Total hydrocarbons (CH_4 equivalent)	-[c]
Ethylene dichloride	Direct chlorination of ethylene	Absorption	Ethylene	3.10[e]
			Ethylene dichloride	2.20[e]
			Hydrogen chloride	0.01[e]
			Ethylene trichloride	0.01[e]
			Other hydrocarbons	0.01
			Total hydrocarbons (CH_4 equivalent)	4.22
Phosgene	Direct chlorination of carbon monoxide	Absorption	Phosgene	0.01[f]
			Carbon monoxide	0.01[f]
			Toluene	1.25[d]
			Total hydrocarbons (CH_4 equivalent)	1.52
		Waste disposal	Phosgene	0.01[f]
			Hydrogen chloride	0.01[f]
			Total hydrocarbons (CH_4 equivalent)	-[c]
Monochlorobenzene and dichlorobenzene	Direct chlorination of benzene	Absorption	Hydrogen chloride/ chlorine	0.06[g]
			Monochlorobenzene	0.03[g]
			Dichlorobenzene	<0.001[g]
			Benzene	0.002[g]
			Other hydrocarbons	<0.001[g]
			Total hydrocarbons (CH_4 equivalent)	0.029

[a] MRC sampling report - carbon tetrachloride by direct chlorination of methane.

[b] Correspondence, J. R. Hofts, FMC Corporation, South Charleston, West Virginia, November 10, 1976.

[c] Not reported.

[d] Reference 15.

[e] Reference 3.

[f] Engineering estimate.

[g] MRC sampling report - Monochlorobenzene by direct chlorination of benzene.

TABLE 11. EMISSION FACTORS BY UNIT OPERATION FOR PROCESSES USING HYDROCHLORINATION

Product	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg
Methyl chloride, methylene chloride, chloroform, carbon tetrachloride	Hydrochlorination of methanol	-[a]	No reported atmospheric emission	-[a]
Ethyl chloride	Hydrochlorination of ethylene	Separation	Ethane	2.5[b]
			Ethyl chloride	2.5[b]
			Dichloroethane	6.0[b]
			Chlorine	0.0005[b]
			Hydrogen chloride	0.0005[b]
			Methane	2.5[b]
			Ethylene	2.5[b]
			Total hydrocarbons (CH_4 equivalent)	11.2
1,1,1-Trichloroethane	Hydrochlorination of vinyl chloride	Heat transfer	Dichloroethane	8.50[c]
			Trichloroethane	9.00[c]
			Hydrogen chloride	0.01[d]
			Other hydrocarbons	0.01[d]
			Total hydrocarbons (CH_4 equivalent)	4.9
		Separation	Dichloroethane	0.50[c]
			Trichloroethane	0.50[c]
			Hydrogen chloride	0.01[d]
			Vinyl chloride	0.50[c]
			Other hydrocarbons	0.01[d]
			Total hydrocarbons (CH_4 equivalent)	0.54

[a] Not applicable.

[b] Reference 15.

[c] Reference 20.

[d] Engineering estimate.

TABLE 12. EMISSION FACTORS BY UNIT OPERATIONS FOR PROCESSES USING OXYHYDROCHLORINATION

Product	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg
Ethylene dichloride	Oxyhydrochlorination of ethylene	Absorption	Chlorine/hydrogen chloride	0.0019[a]
			Carbon tetrachloride	<0.003[a]
			Methane	0.988
			Ethylene	0.332
			Chloroform	<0.005
			Ethylene dichloride	0.46
			Methylene chloride	<0.003
			Vinyl chloride	0.01
			Trichloroethane	<0.005
			Total hydrocarbons (CH_4 equivalent)	1.52
		Separation	Ethylene	0.00001[a]
			Chlorine/hydrogen chloride	0.005[a]
			Ethylene dichloride	0.085[a]
			Methylene chloride	0.0015[a]
			Vinyl chloride	0.012[a]
			Chloroform	0.042[a]
			Carbon tetrachloride	0.094[a]
			Ethyl chloride	0.047[a]
			1,1-Dichloroethane	0.004[a]
			Methane	0.000004
			Vinylidene chloride	0.00009
			Dichloroethylene	0.0008
			Total hydrocarbons (CH_4 equivalent)	0.064
Trichloroethylene	Oxyhydrochlorination of ethylene dichloride	Absorption	Ethylene dichloride	13.0[b]
			Trichloroethylene	8.5[b]
			Carbon tetrachloride	13.0[b]
			Total hydrocarbons (CH_4 equivalent)	6.3

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[a] MRC sampling report - ethylene dichloride by oxyhydrochlorination of ethylene.

[b] Reference 15.

TABLE 13. EMISSION FACTORS BY UNIT OPERATIONS FOR PROCESSES USING CHLOROHYDRINATION

Product	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg
Epichlorohydrin	Chlorohydrination of allyl chloride	Absorption	Allyl chloride	2.00[a]
			Chlorine	0.0005[a]
			Hydrogen chloride	0.0005[a]
			Total hydrocarbons (CH_4 equivalent)	1.2
		Separation	Allyl chloride	2.00[a]
			Chlorine	0.0005[a]
			Trichloropropane	0.50[a]
			Hydrogen chloride	0.0005[a]
			Epichlorohydrin	1.50[a]
			Total hydrocarbons (CH_4 equivalent)	2.13
Propylene oxide	Chlorohydrination of propylene	Absorption	Hydrogen chloride/ chlorine	3.73[b]
			Methane	26.7[b]
			Dichloropropane	8.42[b]
			Ethene	108[b]
			Epichlorohydrin	1.54[b]
			Trichloropropane	0.405[b]
			Bis(β-chloroisopropyl) ether	2.03[b]
			Naphthalene	0.08[b]
			Other hydrocarbon	0.10[b]
			Total hydrocarbons (CH_4 equivalent)	155

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[a] Reference 20.

[b] MRC sampling report - chlorohydrination of propylene.

D. DEFINITION OF A REPRESENTATIVE SOURCE

For the purpose of assessing the environmental impact of the chlorinated hydrocarbon industry, four representative plants were defined based on the four basic processes used by the industry. The parameters used to define a representative plant include process type, population density around the plant site, plant capacity, unit operations used, and average emission rate for total hydrocarbons. Table 14[20,24,31,42,a] summarizes the parameters used for determining a representative plant. For each manufacturing process type, the population density for a representative plant is a capacity weighted average of the population densities of the counties where the plants are located. The representative plant capacity is the average capacity of the existing plants under each process type. The hydrocarbon emission factors are derived from those presented in Tables 10 through 13 by using a capacity weighted average.

E. ENVIRONMENTAL EFFECTS

1. Determination of Severity

a. Maximum Ground Level Concentration--
The maximum ground level concentration, χ_{max}, for each material emitted from each unit operation for each manufacturing process was estimated by Gaussian plume dispersion theory. The maximum ground level concentration, χ_{max} (in g/m^3), was calculated using the equation:

$$\chi_{max} = \frac{2Q}{\pi H^2 e \bar{u}} \qquad (57)$$

where Q = mass emission rate, g/s
H = effective emission height, m
e = 2.72
π = 3.14
$\bar{u}$ = average wind speed (= 4.47 m/s)

b. Time-Averaged Maximum Ground Level Concentration--
$\bar{\chi}_{max}$, the time-averaged maximum ground level concentration calculated from χ_{max}. The averaging time is 24 hr for noncriteria pollutants (chemical substances). For criteria pollutants, averaging times are the same as those used in the primary ambient air quality standards; e.g., 3 hr for hydrocarbons and 24 hr for particulates. The relationship between χ_{max} and $\bar{\chi}_{max}$ is expressed as:

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[a] Information also obtained by personal communication from J. R. Hofts, FMC Corporation, South Charleston, West Virginia, November 10, 1976; and from R. A. Coales, Mobay Chemical Corporation, New Martinsville, West Virginia, April 1, 1976.

TABLE 14. SUMMARY OF CRITERIA USED TO DEFINE REPRESENTATIVE CHLORINATED HYDROCARBON PLANTS

Criterion	Process			
	Direct chlorination	Hydrochlorination	Oxyhydrochlorination	Chlorohydrination
Population density, persons/km^2	277	160	198	333
Capacity, metric tons/yr	77,284	41,465	250,706	122,470
Unit operations used, %				
Absorption	100	33	100	100
Drying	55	33	–[a]	–[a]
Extraction	9	–[a]	–[a]	50
Fluid flow	100	100	100	100
Heat transfer	91	67	100	–[a]
Material handling	100	100	100	100
Mixing	73	33	50	–[a]
Separation	91	100	100	100
Storage	100	100	100	100
Waste disposal	100	100	100	100
Hydrocarbon emission factor, g/kg	2.78	8.62	1.87	123

[a] Unit operation not used.

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_0}{t}\right)^{0.17} \tag{58}$$

where t_0 = short-term averaging time (= 3 min)
t = averaging time, min

c. Source Severity--
To obtain a quantitative measure of the hazard potential of the emission source, the source severity, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} \tag{59}$$

where $\bar{\chi}_{max}$ is the maximum time-averaged ground level concentration of each pollutant and F is defined as the primary ambient air quality standard for criteria pollutants; i.e., particulates, SO_x, NO_x, CO, and hydrocarbons.[a] For noncriteria pollutants:

$$F = TLV \cdot \frac{8}{24} \cdot \frac{1}{100} \tag{60}$$

where TLV (threshold limit value) represents the airborne concentration of a substance under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. The factor 8/24 adjusts the TLV to a continuous rather than work day exposure, and the factor 1/100 accounts for the fact that the general population is a higher risk group than healthy workers. Thus $\bar{\chi}_{max}/F$ represents the ratio of the maximum mean ground level concentration to the concentration constituting an incipient hazard potential.

Because actual production data by plant are unavailable, and to illustrate the worst case hypothetical situation, total capacities were used to calculate emission rate, maximum ground level concentration, time-averaged maximum ground level concentration, source severity, industry contribution to state and national emissions, affected population, and affected area. As shown in Table 1, an average of 74% of the total capacity was utilized in 1975; hence, actual emissions could be as much as 26% lower.

Tables 15, 16, 17, and 18 contain emission rates, maximum ground level concentrations, time-averaged maximum ground level concentrations, and source severities of materials emitted from the unit

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[a] There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is a recommended guideline for meeting the primary ambient air quality standard for oxidants.

TABLE 15. SOURCE SEVERITY: DIRECT CHLORINATION PROCESS

Source type	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg	Average plant capacity, metric tons/yr	Emission height, m	Emission rate, g/s	χ_{max}, g/m³	$\bar{\chi}_{max}$, g/m³	Source severity
Methyl chloride methylene chloride, chloroform, and carbon tetrachloride	Direct chlorination of methane	Absorption	Total hydrocarbons (CH_4 equivalent)	0.012	52,475	25.00	0.020	1.67×10^{-6}	5.85×10^{-7}	0.0037
Carbon tetrachloride	Direct chlorination of carbon disulfide	Absorption	Carbon tetrachloride	2.57	75,598	21.49	6.16	6.99×10^{-4}	2.45×10^{-4}	1.13
			Total hydrocarbons (CH_4 equivalent)	-[a]						
		Separation	Carbon disulfide	2.00	75,598	21.43	4.79	5.47×10^{-4}	1.91×10^{-4}	0.96
			Carbon tetrachloride	0.25		21.43	0.60	6.85×10^{-5}	2.40×10^{-5}	0.32
			Chlorine	0.00015		21.43	0.00036	4.10×10^{-8}	1.43×10^{-8}	0.0014
			Sulfur monochloride	1.00		21.43	2.4	2.74×10^{-4}	9.58×10^{-5}	-[b]
			Total hydrocarbons (CH_4 equivalent)	-[a]						
Carbon tetrachloride and perchloroethylene	Direct chlorination of propane	Drying	Chlorine	10.00	23,360	30.48	7.40	4.17×10^{-4}	1.46×10^{-4}	14.60
			Total hydrocarbons (CH_4 equivalent)	-[a]						
Ethylene dichloride	Direct chlorination of ethylene	Absorption	Ethylene	3.10	352,670	28.55	34.67	2.23×10^{-3}	7.80×10^{-4}	0.19
			Ethylene dichloride	2.20		28.55	24.60	1.58×10^{-3}	5.54×10^{-4}	0.83
			Hydrogen chloride	0.01		28.55	0.11	6.75×10^{-6}	2.36×10^{-6}	0.00132
			Ethylene trichloride	0.01		28.55	0.11	6.75×10^{-6}	2.36×10^{-6}	0.02
			Total hydrocarbons (CH_4 equivalent)	4.22		28.55	47.6	2.92×10^{-3}	1.46×10^{-3}	9.13
Phosgene	Direct chlorination of carbon monoxide	Absorption	Phosgene	0.01	40,118	30.48	0.013	7.16×10^{-7}	2.51×10^{-7}	0.376
			Carbon monoxide	0.01		30.48	0.013	7.16×10^{-7}	2.51×10^{-7}	0.001
			Toluene	1.25		30.48	1.59	8.97×10^{-5}	3.14×10^{-5}	0.0251
			Total hydrocarbons (CH_4 equivalent)	1.52		30.48	1.95	1.05×10^{-4}	5.25×10^{-5}	0.328
		Waste disposal	Phosgene	0.01	40,118	30.48	0.013	7.16×10^{-7}	2.51×10^{-7}	0.376
			Hydrogen chloride	0.01		30.48	0.013	7.16×10^{-7}	2.51×10^{-7}	0.011
			Total hydrocarbons (CH_4 equivalent)	-[a]						
Monochlorobenzene and dichlorobenzene	Direct chlorination of benzene	Absorption	Hydrogen chloride/chlorine	0.06	52,000	20.00	0.10	1.3×10^{-5}	4.6×10^{-6}	0.46
			Monochlorobenzene	0.03		20.00	0.05	6.5×10^{-6}	2.3×10^{-6}	0.002
			Dichlorobenzene	0.001		20.00	0.002	2.6×10^{-7}	9.2×10^{-8}	0.00009
			Benzene	0.002		20.00	0.003	3.9×10^{-7}	1.37×10^{-7}	0.012
			Total hydrocarbons (CH_4 equivalent)	0.03		20.00	0.05	6.25×10^{-6}	3.13×10^{-6}	0.021

[a] Not reported.

[b] TLV not available.

TABLE 16. SOURCE SEVERITY: HYDROCHLORINATION PROCESS

Source type	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg	Average plant capacity, metric tons/yr	Emission rate, g/s	Emission height, m	χ_{max}, g/m³	$\bar{\chi}_{max}$, g/m³	Source severity
Methyl chloride, methylene chloride, chloroform, and carbon tetrachloride	Hydrochlorination of methanol	-[a]	-[a]	-[a]	-[a]	-[a]	-[a]	-[a]	-[a]	-[a]
Ethyl chloride	Hydrochlorination of ethylene	Separation	Ethane	2.5	55,000	4.36	30.48	2.46×10^{-4}	8.6×10^{-5}	1.93×10^{-2}
			Ethylchloride	2.5		4.36	30.48	2.46×10^{-4}	8.6×10^{-5}	9.92×10^{-3}
			Dichloroethane	6.0		10.46	30.48	5.90×10^{-4}	2.06×10^{-4}	0.31
			Chlorine	0.0005		8.7×10^{-4}	30.48	4.90×10^{-8}	1.72×10^{-8}	1.72×10^{-3}
			Hydrogen chloride	0.0005		8.7×10^{-4}	30.48	4.90×10^{-8}	1.72×10^{-8}	7.36×10^{-4}
			Methane	2.5		4.36	30.48	2.46×10^{-4}	8.6×10^{-5}	0.04
			Ethylene	2.5		4.36	30.48	2.46×10^{-4}	8.6×10^{-5}	0.02
			Total hydrocarbons (CH_4 equivalent)	11.2		19.7	30.48	1.11×10^{-3}	5.55×10^{-4}	3.47
1,1,1-Trichloroethane	Hydrochlorination of vinyl chloride	Heat transfer	Dichloroethane	8.50	104,000	28.10	30.48	1.6×10^{-3}	5.5×10^{-4}	0.83
			Trichloroethane	9.00		29.75	30.48	1.7×10^{-3}	5.9×10^{-4}	9.3×10^{-2}
			Hydrogen chloride	0.01		0.033	30.48	1.9×10^{-6}	6.5×10^{-7}	2.8×10^{-2}
			Total hydrocarbons (CH_4 equivalent)	4.9		16.3	30.48	9.3×10^{-4}	4.5×10^{-4}	2.81
		Separation	Dichloroethane	0.50	104,000	1.65	30.48	9.3×10^{-5}	3.3×10^{-5}	4.9×10^{-2}
			Trichloroethane	0.50		1.65	30.48	9.3×10^{-5}	3.3×10^{-5}	5.1×10^{-3}
			Hydrogen chloride	0.01		0.033	30.48	1.9×10^{-6}	6.5×10^{-7}	0.03
			Vinyl chloride	0.50		1.65	30.48	9.3×10^{-5}	3.3×10^{-5}	3.81
			Total hydrocarbons (CH_4 equivalent)	0.54		1.80	30.48	1.00×10^{-4}	5.0×10^{-5}	0.31

[a] No reported atmospheric emission.

[b] TLV not available.

TABLE 17. SOURCE SEVERITY: OXYHYDROCHLORINATION PROCESS

Source type	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg	Average plant capacity metric tons/yr	Emission rate, g/s	Emission height, m	χ_{max}, g/m³	$\bar{\chi}_{max}$, g/m³	Source severity
Ethylene dichloride	Oxyhydrochlorination of ethylene	Absorption	Chlorine/hydrogen chloride	0.0019	340,000	0.021	55.00	3.6×10^{-7}	1.3×10^{-7}	0.013
			Carbon tetrachloride	<0.03		0.032	55.00	5.4×10^{-7}	1.9×10^{-7}	8.6×10^{-4}
			Methane	0.988		10.7	55.00	1.8×10^{-4}	6.3×10^{-5}	0.027
			Ethylene	0.332		3.6	55.00	6.1×10^{-5}	2.1×10^{-5}	0.005
			Chloroform	<0.005		0.005	55.00	8.5×10^{-7}	3.0×10^{-7}	7.5×10^{-4}
			Ethylene dichloride	0.46		5.0	55.00	8.5×10^{-5}	3.0×10^{-5}	0.04
			Methylene chloride	<0.003		0.032	55.00	5.4×10^{-7}	1.9×10^{-7}	7.9×10^{-5}
			Vinyl chloride	0.01		0.11	55.00	1.9×10^{-6}	6.7×10^{-7}	0.077
			Trichloroethane	0.005		0.05	55.00	8.5×10^{-7}	3.0×10^{-7}	4.7×10^{-5}
			Total hydrocarbons (CH_4 equivalent)	1.52		16.4	55.00	2.7×10^{-4}	1.4×10^{-4}	0.88
		Separation	Chlorine/hydrogen chloride	0.005		0.054	16.00	1.1×10^{-5}	3.9×10^{-6}	0.39
			Ethylene	0.0001		0.0001	16.00	2.0×10^{-8}	7.0×10^{-9}	1.7×10^{-6}
			Ethylene dichloride	0.085		0.92	16.00	1.8×10^{-4}	6.3×10^{-5}	0.094
			Methylene chloride	0.0015		0.016	16.00	3.2×10^{-6}	1.1×10^{-6}	4.6×10^{-4}
			Vinyl chloride	0.012		0.13	16.00	2.6×10^{-5}	9.1×10^{-6}	1.0
			Chloroform	0.042		0.45	16.00	9.0×10^{-5}	3.2×10^{-5}	0.08
			Carbon tetrachloride	0.094		1.02	16.00	2.04×10^{-4}	7.1×10^{-5}	0.32
			Ethyl chloride	0.047		0.51	16.00	1.02×10^{-4}	3.6×10^{-5}	4.1×10^{-3}
			1,1-Dichloroethane	0.004		0.043	16.00	8.6×10^{-6}	3.0×10^{-6}	1.1×10^{-3}
			Methane	0.000004		0.00004	16.00	8.0×10^{-9}	2.8×10^{-9}	1.2×10^{-6}
			Vinylidene chloride	0.0009		0.0010	16.00	2.0×10^{-7}	7.0×10^{-8}	1.3×10^{-6}
			Dichloroethylene	0.008		0.0086	16.00	1.7×10^{-6}	6.0×10^{-7}	2.3×10^{-4}
			Total hydrocarbons (CH_4 equivalent)	0.064		0.70	16.00	1.4×10^{-4}	7.0×10^{-5}	0.44
Trichloroethylene	Oxyhydrochlorination of ethylene dichloride	Absorption	Ethylene dichloride	13.0	50,000	20.60	30.48	1.2×10^{-3}	4.1×10^{-4}	0.61
			Trichloroethylene	28.5		45.16	30.48	2.5×10^{-3}	8.9×10^{-4}	0.50
			Carbon tetrachloride	13.0		20.60	30.48	1.2×10^{-3}	4.1×10^{-4}	1.88
			Total hydrocarbons (CH_4 equivalent)	6.3		10.08	30.48	5.6×10^{-4}	2.9×10^{-4}	1.81

TABLE 18. SOURCE SEVERITY: CHLOROHYDRINATION PROCESS

Source type	Manufacturing process	Unit operation	Material emitted	Emission factor, g/kg	Average plant capacity metric tons/yr	Emission rate, g/s	Emission height, m	χ_{max}, g/m³	$\bar{\chi}_{max}$, g/m³	Source severity
Epichlorohydrin	Chlorohydrination of allyl chloride	Absorption	Allyl chloride	2.00	68,000	4.31	30.48	2.43×10^{-4}	8.51×10^{-5}	8.51
			Chlorine	0.0005		0.0011	30.48	6.20×10^{-8}	2.17×10^{-8}	0.00217
			Hydrogen chloride	0.0005		0.0011	30.48	6.20×10^{-8}	2.17×10^{-8}	0.00093
			Total hydrocarbons (CH_4 equivalent)	1.2		2.59	30.48	1.46×10^{-4}	7.32×10^{-5}	0.46
		Separation	Allyl chloride	2.00	68,000	4.31	30.48	2.43×10^{-4}	8.51×10^{-5}	8.51
			Chlorine	0.0005		0.0011	30.48	6.20×10^{-8}	2.17×10^{-8}	0.00217
			Trichloropropane	0.50		1.08	30.48	6.01×10^{-5}	2.13×10^{-5}	0.0213
			Hydrogen chloride	0.0005		0.0011	30.48	6.20×10^{-8}	2.17×10^{-8}	0.00093
			Epichlorohydrin	1.50		3.24	30.48	1.83×10^{-4}	6.40×10^{-5}	1.01
			Total hydrocarbons (CH_4 equivalent)	2.13		4.57	30.48	2.58×10^{-4}	1.29×10^{-4}	0.81
Propylene oxide	Chlorohydrination of propylene	Absorption	Hydrogen chloride/ chlorine	3.73	155,128	18.3	50.00	3.6×10^{-4}	1.3×10^{-4}	13
			Methane	26.7		130	50.00	2.6×10^{-3}	9.1×10^{-4}	0.40
			Dichloropropane	8.42		41.2	50.00	8.2×10^{-4}	2.9×10^{-4}	0.24
			Ethene	108		530	50.00	1.1×10^{-2}	3.9×10^{-3}	0.91
			Epichlorohydrin	1.54		7.5	50.00	1.5×10^{-4}	5.3×10^{-5}	0.84
			Trichloropropane	0.405		1.98	50.00	4.0×10^{-5}	1.4×10^{-5}	0.014
			Bis(β-chloro-isopropyl) ether	2.03		9.9	50.00	1.9×10^{-4}	6.7×10^{-5}	20.3
			Naphthalene	0.08		0.39	50.00	7.8×10^{-6}	2.7×10^{-6}	0.016
			Other hydrocarbons	0.10		0.49	50.00	9.8×10^{-6}	3.4×10^{-6}	0.02
			Total hydrocarbons (CH_4 equivalent)	155		760	50.00	1.5×10^{-2}	7.5×10^{-3}	47

[a] TLV not available.

TABLE 19. SOURCE SEVERITY: REPRESENTATIVE DIRECT CHLORINATION, HYDROCHLORINATION, OXYHYDROCHLORINATION, AND CHLOROHYDRINATION PROCESSES

Manufacturing process	Material emitted	Emission factor, g/kg	Emission rate, g/s	Emission height, m	χ_{max}, g/m³	$\bar{\chi}_{max}$, g/m³	Source severity
Chlorination	Hydrocarbons	2.78	6.88	25.1	5.4×10^{-4}	2.7×10^{-4}	1.69
Hydrochlorination	Hydrocarbons	8.62	11.4	30.5	6.1×10^{-4}	3.1×10^{-4}	1.94
Oxydrochlorination	Hydrocarbons	1.87	15.0	33.8	6.6×10^{-4}	3.3×10^{-4}	2.06
Chlorohydrination	Hydrocarbons	123	480	40.2	1.5×10^{-2}	7.5×10^{-3}	46.8

processes of direct chlorination, hydrochlorination, oxyhydrochlorination, and chlorohydrination, respectively. Table 19 presents the source severity of representative processes. For each unit process, the source severities are calculated by source types, manufacturing process, materials emitted, and unit operations involved. The appendix contains the derivations of source severity equations.

2. Industry Contribution to Total Atmospheric Emissions

The mass emissions of criteria pollutants resulting from the manufacture of chlorinated hydrocarbons were calculated for each of the four processes used to produce chlorinated hydrocarbons. Emission factors used in the calculations were obtained from Table 14. The appropriate emission factors were multiplied by the chlorinated hydrocarbon capacity nationwide to obtain the industry contribution to national emissions as shown in Table 20. Similarly, emission factors were multiplied by the statewide capacity of chlorinated hydrocarbons to obtain the industry contribution to statewide emissions as shown in Table 21. The total annual mass emissions of criteria pollutants from all sources nationwide and from sources within appropriate states were obtained from Reference 46. The percentages of the total emissions resulting from chlorinated hydrocarbon manufacture were computed using these values and are also presented in Tables 20 and 21.

TABLE 20. CHLORINATED HYDROCARBON INDUSTRY CONTRIBUTION TO NATIONAL STATIONARY SOURCE EMISSIONS OF CRITERIA POLLUTANTS[46]

		Emissions from the chlorinated hydrocarbon industry							
		Direct chlorination		Hydrochlorination		Oxyhydrochlorination		Chlorohydrination	
Material emitted	Total national emissions, 10^6 metric tons/yr	10^3 metric tons/yr	Percent of national emissions	10^3 metric tons/yr	Percent of national emissions	10^3 metric tons/yr	Percent of national emissions	10^3 metric tons/yr	Percent of national emissions
Hydrocarbons	25	14.6	0.06	9.95	0.04	6.10	0.024	120	0.48

3. Affected Population and Affected Area

A measure of the population which is exposed to a high contaminant concentration (S 0.05, 0.1, and ≥1.0) due to a representative chlorinated hydrocarbon plant can be obtained as follows. The values of x, the distance from the source, for which

$$\frac{\overline{\chi}(x)}{F} = 0.1 \qquad (61)$$

TABLE 21. CHLORINATED HYDROCARBON INDUSTRY CONTRIBUTIONS TO STATE EMISSIONS OF HYDROCARBONS[46]

State	State hydrocarbon emissions, 10^3 metric tons	Direct chlorination			Hydrochlorination			Oxyhydrochlorination			Chlorohydrination		
		State capacity, 10^3 metric tons	Emissions, metric tons	Percent	State capacity, 10^3 metric tons	Emissions, metric tons	Percent	State capacity, 10^3 metric tons	Emissions, metric tons	Percent	State capacity, 10^3 metric tons	Emissions, metric tons	Percent
Alabama	643.4	102.1	283.8	0.044									
California	2,161.0	47.2	131.2	0.006	45.4	391.3	0.018	156.2	292.8	0.014			
Delaware	63.9	90.7	252.1	0.395									
Illinois	1,826.0	64.9	180.4	0.010									
Indiana	600.5	27.2	75.62	0.0126									
Kansas	309.6	65.8	182.9	0.059	15.9	-[a]	-[a]						
Kentucky	326.3	83.9	233.2	0.071	9.1	-[a]	-[a]	459.4	861.3	0.26	59.0	7,260	2.2
Louisiana	1,920.0	2,506.0	6,970	0.36	569.7	4,910	0.26	1,032.3	1,935	0.10	181.4	22,300	1.2
Maryland	295.9	2.72	7.56	0.0026									
Michigan	717.9	167.8	466.5	0.065	6.8	-[a]	-[a]				79.4	9,780	1.4
Nevada	53.7	31.8	88.40	0.16									
New Jersey	819.5	61.2	170.1	0.021	49.9	430.1	0.052						
New York	1,262.0	111.6	310.2	0.025	22.7	-[a]	-[a]						
Ohio	1,153.0	25.0	69.5	0.006									
Texas	2,219.0	1,471.9	4,090	0.18	344.7	2,971	0.13	1,611.3	3,020	0.14	660.0	81,300	3.7
West Virginia	116.2	395.5	1,099	0.95	145.2	1,251	1.08		6,109			120,600	
Total			14,610			9,953							

Note.—Blanks indicate that process not used in state.

[a] No reported emissions.

are determined by iteration. The value of $\bar{\chi}(x)$, the annual mean ground level concentration, is computed from the equation:

$$\bar{\chi}\ (x) = \frac{2.03\ Q}{\sigma_z \bar{u} x} \exp \; -\frac{1}{2}\,\frac{H}{\sigma_z}^{\;2} \qquad (62)$$

where Q = emission rate, g/s
H = effective emission height, m
$\bar{x}$ = downwind distance from source, m
$\bar{u}$ = average wind speed (= 4.5 m/s)
σ_z = vertical dispersion coefficient, m

For atmospheric stability class C (neutral conditions), σ_z is given by:[47]

$$\sigma_z = 0.113x^{0.911} \qquad (63)$$

The affected area is then computed as

$$A = \pi(x_2{}^2 \quad x_1{}^2),\ \text{km}^2 \qquad (64)$$

where x_1 and x_2 are the two roots of Equation 62.

The (capacity weighted) mean population density, $\bar{D}_P$, is calculated as follows:

$$\bar{D}_P = \frac{\sum_i C_i D_{P_i}}{\sum_i C_i},\ \text{persons/km}^2 \qquad (65)$$

where C_i = production capacity of plant i
D_{P_i} = county population density for plant i

The product $A \cdot \bar{D}_P$ is designated the "affected population."

The affected areas and affected populations were calculated for the hydrocarbon emission from representative plants using direct chlorination, hydrochlorination, oxyhydrochlorination, and are reported in Table 22 for S ≥0.05, 0.1 and 1.0.

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[47] Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11):859-863, 1972.

TABLE 22. AFFECTED POPULATION AND AFFECTED AREA

Manufacturing process	Affected area, km^2			Affected population, persons		
	S≥0.05	≥0.1	≥1.0	≥0.05	≥0.1	≥1.0
Direct chlorination	21.4	10.2	0.57	5,923	2,820	158
Hydrochlorination	36	17.3	1.0	5,812	2,772	167
Oxyhydrochlorination	48.5	23.1	1.45	9,600	4,580	286
Chlorohydrination	1,850	894	79.4	615,000	297,600	26,400

4. Growth Factor

In 1975, 8.52 x 10^6 metric tons of the 14 chlorinated hydrocarbons listed previously in Table 1 were produced in the United States. Production in 1980 is expected to total 10.4 x 10^6 metric tons. Assuming that the same level of control technology exists in 1980 as existed in 1975, the emissions from the chlorinated hydrocarbon industry will increase by 20% over that period; i.e.,

$$\frac{\text{Emissions in 1980}}{\text{Emissions in 1975}} = \frac{10.4}{8.52} = 1.2$$

For individual chemicals emission increases or decreases should follow production trends projected in Section VI.

SECTION V

CONTROL TECHNOLOGY

Emissions from the manufacture of chlorinated hydrocarbons consist primarily of hydrocarbons. Control techniques applicable to hydrocarbon emission sources include:

- Absorption
- Condensation
- Incineration
- Adsorption

Other areas warranting controls include:

- Control of storage tank emissions
- Control of fugitive emissions
- Waste disposal

A. ABSORPTION

Absorption is the process by which one or more soluble components are removed from a gas mixture by dissolution in a relatively nonvolatile liquid. The absorption process may consist of dissolving the component in the nonvolatile liquid followed by reaction with the liquid or simply dissolving without reaction.[48] This control technology is common within the chlorinated hydrocarbon manufacturing industry. Absorption is used primarily to control hydrogen chloride and chlorine vapors rather than hydrocarbons, because low concentrations of hydrocarbon vapors require long contact time and large quantities of absorbent.[49] When absorption is used to control hydrocarbon vapors, the solution must be used as a process makeup stream or the absorbent must be regenerated. Otherwise, the absorbent stream presents an additional waste disposal problem. Absorption is also used in conjunction with other control techniques such as incineration or adsorption to achieve a greater degree of emission control than these techniques alone provide.[49]

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[48] Hughes, T. W., D. A. Horn, C. W. Sandy, and R. W. Serth. Source Assessment: Prioritization of Air Pollution for Industrial Surface Coating Operations. EPA-650/2-75-019-a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1975. 303 pp.

[49] Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources. Publication No. AP-68, U.S. Department of Health, Education, and Welfare, Washington, D.C., March 1970. pp. 3-1 through 3-26.

Absorption is an important processing step in the chlorinated hydrocarbon industry. Products absorbed in a product recovery step in industrial processes include hydrocarbons, chlorine, and hydrogen chloride. Absorption has also been employed in scrubbing to remove unreacted raw materials from the main process vent.[49]

The ideal absorption system should meet the following requirements:

- The gas should be readily soluble to increase absorption rate and decrease the quantity of absorbent required. Solvents chemically similar to the solute generally provide good solubility.
- The solvent should be nonvolatile, noncorrosive (to reduce equipment costs), readily available, and inexpensive.
- The solvent should have low viscosity to increase absorption and reduce flooding.
- The solvent should be low in toxicity, nonflammable, chemically stable, and have a low freezing point.

The common absorbents for chlorine and hydrogen chloride are water, sodium carbonate and sodium hydroxide, and for hydrocarbons, nonvolatile hydrocarbon oils.[49]

Absorption equipment provides good contact between the gas and liquid solvent to permit interphase diffusion of the materials. Types of equipment providing contact include bubble plate columns, packed towers, spray towers, and venturi scrubbers.[48] Figures 15, 16, 17, and 18 show diagrams of a bubble-cap tray tower, packed tower, venturi scrubber, and spray tower, respectively.[49]

In the bubble plate column, a number of plates or trays are arranged so that the gas is dispersed through a layer of solvent on each plate. Each plate acts as a separate stage, and the number of plates used depends upon the difficulty of the mass transfer operation and the degree of separation required. A packed tower is filled with a packing material having a large surface-to-volume ratio. The packing material is wetted by the solvent to provide a large surface area of liquid film for continuous contacting of the gases. In a spray tower, the liquid is sprayed and the gas mixture is passed through the spray. In a venturi scrubber, gas and solvent come into contact in the throat of the venturi nozzle. The gas-liquid mixture then enters an entrainment separator tangentially, and centrifugal force separates the liquid droplets from the gas.[49]

Absorption of a gaseous component by a liquid occurs when the liquid contains less than the equilibrium concentration of the component. This departure of the liquid stream from equilibrium

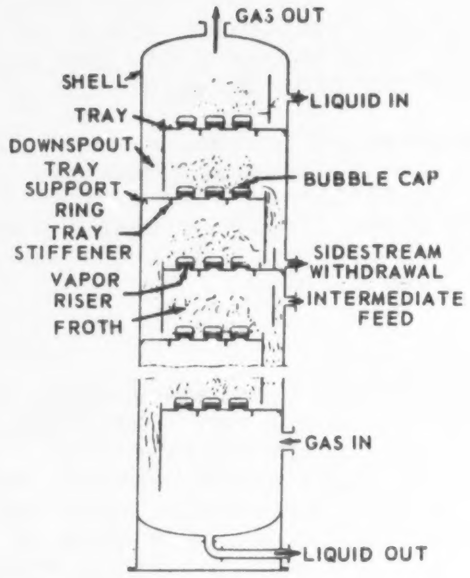
GAS OUT
SHELL
TRAY
DOWNSPOUT
TRAY SUPPORT RING
TRAY STIFFENER
VAPOR RISER
FROTH
LIQUID IN
BUBBLE CAP
SIDESTREAM WITHDRAWAL
INTERMEDIATE FEED
GAS IN
LIQUID OUT

Figure 15. Schematic diagram of a bubble-cap tray tower.[49]

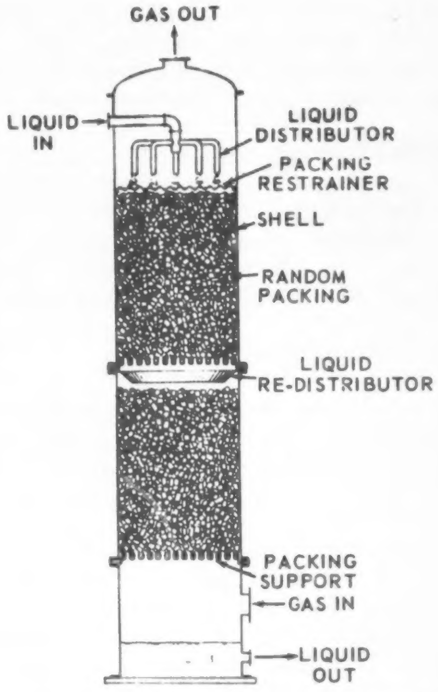
GAS OUT
LIQUID IN
LIQUID DISTRIBUTOR
PACKING RESTRAINER
SHELL
RANDOM PACKING
LIQUID RE-DISTRIBUTOR
PACKING SUPPORT
GAS IN
LIQUID OUT

Figure 16. Packed tower.[49]

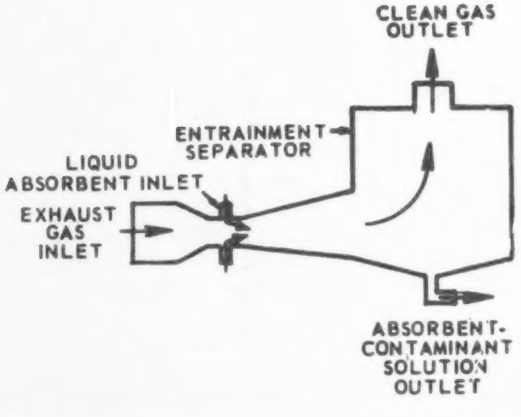
CLEAN GAS OUTLET
ENTRAINMENT SEPARATOR
LIQUID ABSORBENT INLET
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET

Figure 17. Venturi scrubber.[49]

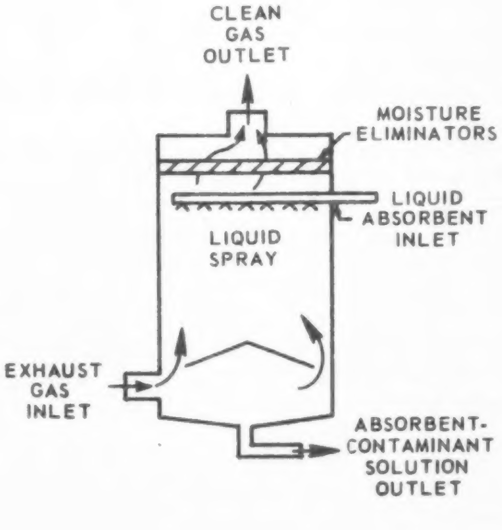
CLEAN GAS OUTLET
MOISTURE ELIMINATORS
LIQUID ABSORBENT INLET
LIQUID SPRAY
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET

Figure 18. Spray tower.[49]

provides the driving force for absorption. The absorption rate depends upon the temperature, diffusivity, viscosity, and density of the substance, the tower conditions--particularly the gas and liquid mass flow rates--and the type of packing material.

The design of absorbers has been discussed by Treybal[50] and Perry and Chilton.[51] The problems which arise in designing absorbers can be attributed to variation of solubilities because of non-isothermal operating conditions, semi-ideal liquid solutions, and the change in the gas and liquid flow rates caused by transfer of the solute from the gas phase to the liquid phase.

B. CONDENSATION

Hydrocarbons can be removed from a gas stream by condensation. Because of their relatively high boiling points, many hydrocarbons readily condense even though they are not highly concentrated. A hydrocarbon vapor will condense when, at a given temperature, the partial pressure of the compound is equal to or greater than its vapor pressure. Alternatively, if the temperature of a gaseous mixture is reduced to the saturation temperature (the temperature at which the vapor pressure equals the partial pressure of one of the constituents), condensation will also occur. Thus either increasing the system pressure or decreasing the temperature can cause condensation. In most air pollution control applications, decreased temperature is used to condense hydrocarbons, since increased pressure is usually impractical.[49]

Condensers have found a wide range of application in the chlorinated hydrocarbon industry where their purpose has been to condense concentrated vapors in the process rather than to reduce atmospheric emissions, although they are used for the latter purpose. When applied in the process, condensers recover valuable products and reduce the volume of effluent gas.[49]

The equilibrium partial pressure limits the control of organic emissions by condensation. As condensation occurs, the partial pressure of material remaining in the gas decreases rapidly, preventing complete condensation. For example, even at 0°C, toluene has a vapor pressure of approximately 800 Pa (6 mm Hg). At atmospheric pressure of 101.3 kPa (760 mm Hg), a gas stream saturated with toluene would still contain about 8,000 ppm of that gas. Thus, to achieve a high degree of overall efficiency, a condenser must usually be followed by a secondary air pollution control device such as an afterburner.[49]

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[50] Treybal, R. E. Mass Transfer Operations. McGraw-Hill Book Company, New York, New York, 1968. 666 pp.

[51] Chemical Engineers Handbook, Fifth Edition, J. H. Perry and C. H. Chilton, eds. McGraw-Hill Book Company, New York, New York, 1973.

Condensation is usually achieved by lowering the vapor temperature. Thus condensation is induced by deploying a cold surface or a cooling liquid.[49] There are basically two types of condensers--surface and contact--used for condensation. In a surface condenser, the vapor to be condensed and the cooling medium are separated by a metal wall; in a contact condenser, the vapor and the cooling medium are brought into direct contact.[49]

Surface condensers include the common shell and tube-type heat exchangers, where the cooling medium, usually water, flows through the tubes, and the vapor condenses on the outside surface of the tubes; i.e., in the shell. The condensed vapor forms a film on the cold tubes and can be drained for storage or disposal. Air-cooled condensers are usually constructed with finned tubes, and the vapor condenses inside the tubes.[49]

In contact condensers, the vapor is cooled by direct spraying of the gas stream with a cold liquid, usually water. The mixture of water and condensed vapor obtained may be discarded or recovered. Contact condensers generally are less expensive, more flexible, and more efficient in removing hydrocarbons than surface condensers. Types of contact condensers include spray tower, steam or water ejector, and barometric condensers. Figures 19 through 26 show different types of surface and contact condensers.

When hydrocarbons are being condensed, important design considerations of condensers include the type(s) of compounds to be condensed and their temperature, volume, concentration, vapor pressure, and specific heat. For surface condensers, it is important to know the heat transfer coefficients on both the vapor and the liquid sides, the temperature, and the amount of coolant available. For contact condensers, the amount of cooling water required is a critical design factor.[49]

C. INCINERATION

Because of the formation of noxious compounds (e.g., HCl), incineration alone is seldom used for the control of chlorinated hydrocarbons. An adsorber may be used in conjunction with the incinerator to achieve greater emission control.[52]

1. Thermal Incineration

Direct-flame afterburners depend upon flame contact and high temperatures to burn the combustible material in gaseous effluents to

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[52] Rolke, R. W., R. D. Hawthorne, C. R. Garbett, E. R. Slater, T. T. Phillips, and G. D. Towell. Afterburner Systems Study. EPA-R2-72-062 (PB 212 560), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1972. 336 pp.

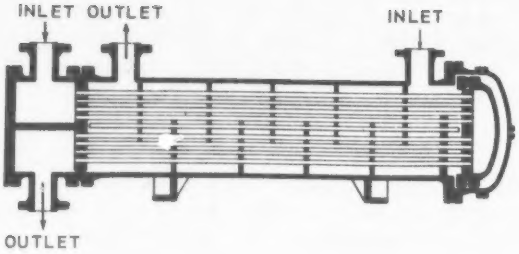
INLET
OUTLET
INLET
OUTLET

Figure 19. Surface condenser: shell and tube.

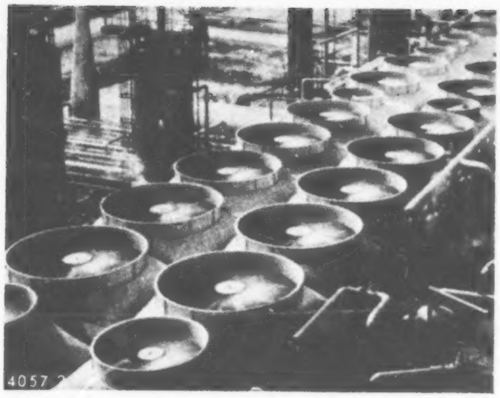

Figure 20. Surface condenser: fin fan.

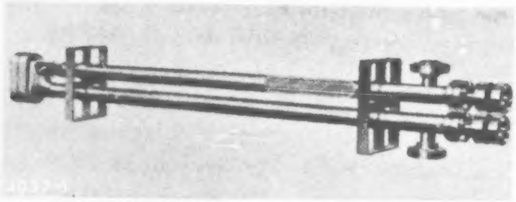

Figure 21. Surface condenser: finned hairpin section.

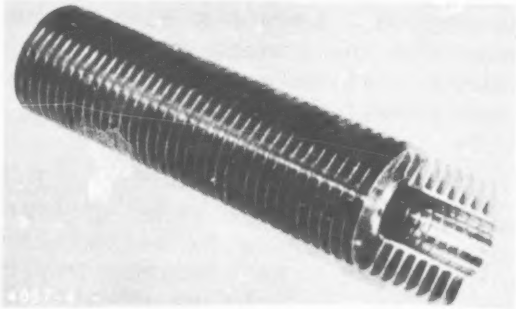

Figure 22. Surface condenser: integral finned section.

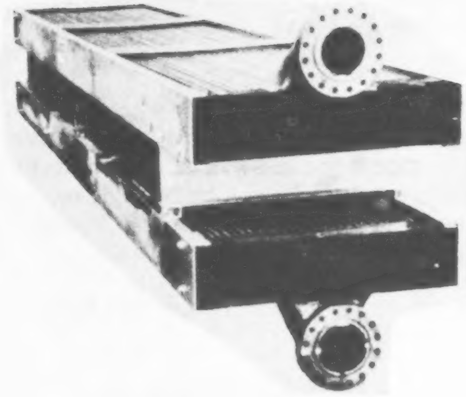

Figure 23. Surface condenser: tubular.

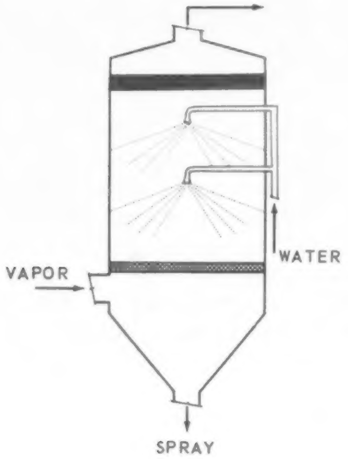
WATER
VAPOR
SPRAY

Figure 24. Contact condenser: spray.

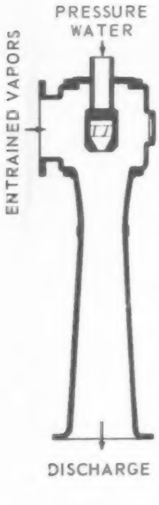
PRESSURE WATER
ENTRAINED VAPORS
DISCHARGE

Figure 25. Contact condenser: jet

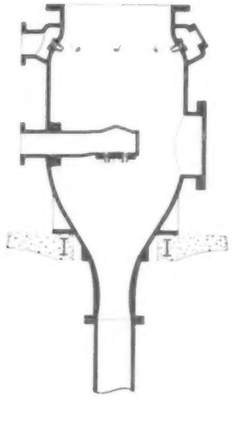

Figure 26. Contact condenser: barometric.

form carbon dioxide and water.[52] The combustible materials may be gases, vapors, or entrained particulate matter which contributes opacity, odor, irritants, photochemical reactivity, and toxicity to the effluent. Direct-flame afterburners consist of a refractory-lined chamber, one or more burner temperature indicator-controllers, safety equipment, and, sometimes, heat recovery equipment.[52]

The afterburner chamber consists of a mixing section and a combustion section. The mixing section provides contact between the contaminated gases and the burner flame. Good mixing is provided by high velocity flow which creates turbulence. The combustion section is designed to provide a retention time of 0.3 to 0.5 seconds for completion of the combustion process. Afterburner discharge temperatures range from 540°C to 800°C, depending on the air pollution problem. Higher temperatures result in higher afterburner efficiencies.[52]

The gas burners used in afterburners are of the nozzle-mixing, premixing, multiport, or mixing plate type. Burner placement varies depending on burner type and on the design objective of providing intimate contact of the contaminated air with the burner flames.[52]

Nozzle-mixing and premixing burners are arranged to fire tangentially into a cylindrical afterburner. Several burners or nozzles are required to ensure complete flame coverage, and additional burners or nozzles may be arranged to fire along the length of the burner. Air for fuel combustion is taken from the outside air or from the contaminated air stream, which is introduced tangentially or along the major axis of the cylinders.[52]

Multiport burners are installed across a section of the afterburner separate from the main chamber. Although all air for combustion is taken from the contaminated airstream, multiport burners are not capable of handling all of the contaminated airstream. Contaminated air in excess of that used for fuel combustion must be passed around the burner and mixed with the burner flames in a restricted and baffled area.[52]

Mixing plate burners, developed for afterburner applications, are placed across the inlet section of the afterburner. The contaminated air and the burner flames are mixed by profile plates installed around the burner between the burner and afterburner walls. The high velocities (1 m/s) provided by the burner and profile plate design ensure mixing of the burner flames and the contaminated air not flowing through the burner. The contaminated airstream provides air for fuel combustion.[52]

The efficiency of an afterburner is a function of retention time, operating temperature, flame contact, and gas velocity. No quantitative mathematical relationship exists between these variables because the kinetics of the combustion process are complex, and flow inside afterburners is not defined. However, for good design, the following observations can be made with respect to afterburner efficiency:[52]

- Efficiency increases with increasing afterburner operating temperature.
- Efficiency decreases if the contaminated gases entering the afterburner are excessively preheated.
- Efficiency increases with increasing contact between the contaminated gases and the burner flame.
- Efficiency increases with increasing retention time for retention times less than 1 second.
- Efficiency is a function of the afterburner design and the inlet concentration of organic materials.
- Ninety percent afterburner efficiency is difficult to reach below a 700°C operating temperature if the generation of carbon monoxide in the afterburner is included in the calculation of efficiency.

2. Catalytic Incineration

A catalytic afterburner contains a preheat burner section, a chamber containing a catalyst, temperature indicators and controllers, safety equipment, and heat recovery equipment. The catalyst in such an afterburner promotes combustion by increasing the rate of the oxidation reactions without itself appearing to change chemically.[48] (See Figure 27.)

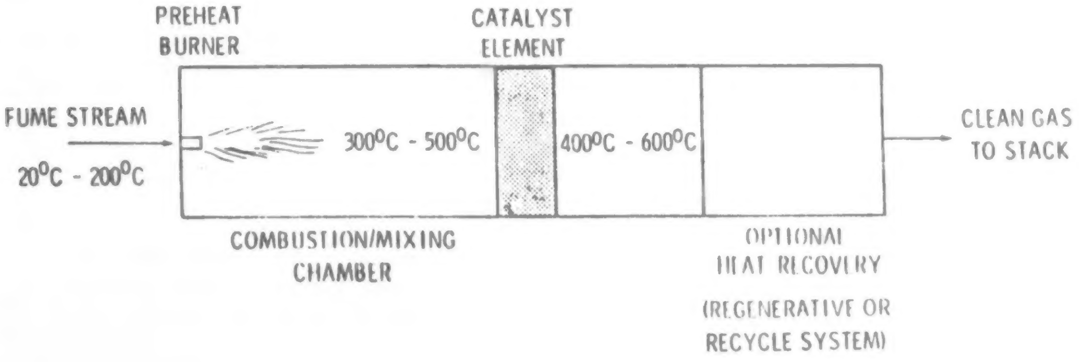
PREHEAT BURNER
CATALYST ELEMENT
FUME STREAM
20°C - 200°C
300°C - 500°C
400°C - 600°C
CLEAN GAS TO STACK
COMBUSTION/MIXING CHAMBER
OPTIONAL HEAT RECOVERY
(REGENERATIVE OR RECYCLE SYSTEM)

Figure 27. Schematic diagram of a catalytic afterburner.[48]

The contaminated air entering a catalytic afterburner is heated to the temperature necessary for carrying out the catalytic combustion. The preheat zone temperature, in the range of 300°C to 500°C, varies with the combustion and type of contaminants. Because of thermal incineration in the preheat zone, the preheat burner can contribute to the efficiency of a catalytic afterburner.[48]

Catalysts used for catalytic afterburners may be platinum-family metals supported on metal or matrix elements made of ceramic honeycombs. Catalyst supports should have high geometric surface area, low pressure drop, structural integrity and durability, and should permit uniform distribution of the flow of the waste stream through the catalyst. Catalysts can be poisoned by phosphorus, bismuth, arsenic, antimony, mercury, lead, zinc, and tin, which are thought to form alloys with the metal catalyst. Catalysts are deactivated by materials which form coatings on them, such as the particulate material, resins, and carbon formed during organic material breakdown. High temperatures will also deactivate catalysts. Because the combustion reaction is exothermic, the catalyst bed temperature is above the inlet temperature. The temperature increase depends on the concentration of organic material burned and the heat of combustion of that material. Compensation for decreased catalyst activity can be made by: (1) initial overdesign in specifying the quantity of catalyst required to attain required performance, (2) increasing preheat temperature as chemical activity decreases, (3) regenerating the catalyst, and (4) replacing the catalyst.[48]

The quantity of catalyst required for 85% to 95% conversion of hydrocarbons ranges from 0.5 m^3 to 2 m^3 of catalyst per 1,000 m^3/min of waste stream. Although the catalyst temperature depends on the hydrocarbon burned and the condition of the catalyst, the operating temperatures of catalytic afterburners range from 400°C to 600°C.[52]

3. Flares

Flares are used for the combustion of low concentration chlorinated hydrocarbon streams and intermittent emissions caused by plant upset. Flares are not considered an ideal form of control. Their usefulness is limited because:[45]

- Oxidation of chlorinated hydrocarbons produces hydrogen chloride which itself is a pollutant.
- Dilute gas streams cannot support combustion, and small changes in vent gas composition can extinguish the burner unless supplemental fuel and adequate instrumentation are provided.
- Heat produced is wasted.
- Improper firing of the burner can result in operating temperatures which favor NO_x formation.

- Efficiency for removing contaminants is less than that of other combustion devices.

D. ADSORPTION

Adsorption is a mechanism for removing molecules from a liquid or gas by contacting them with a solid. Gases, liquids, or solids can be selectively removed from airstreams with materials known as adsorbents. The material which adheres to the adsorbent is called the adsorbate.[48]

The mechanism by which components are adsorbed is complex, and although adsorption occurs at all solid interfaces, it is minimal unless the adsorbent has a large surface area, is porous, and possesses capillaries. The important characteristic of solid adsorbents are their large surface-to-volume ratio and preferential affinity for individual components.[48]

The adsorption process includes three steps. The adsorbent is first contacted with the fluid, and adsorption results. Second, the unadsorbed portion of the fluid is separated from the adsorbent. For gases, this operation is completed when the gases leave the adsorbent bed. Third, the adsorbent is regenerated by removal of the adsorbate. Low pressure steam is used to regenerate the adsorbent, and the condensed vapors are separated from the water by decantation, distillation, or both.[48]

Activated carbon is capable of adsorbing 95% to 98% of the organic vapor from air at ambient temperature in the presence of water in the gas stream.[53] When an organic vapor in air mixture starts to pass over activated carbon, complete adsorption of the organic vapor takes place. As the adsorptive capacity of the activated carbon is approached, traces of vapor appear in the exit air, indicating that the breakpoint of the activated carbon has been reached. As the air flow is continued and although additional amounts of organic materials are adsorbed, the concentration of organic vapor in the exit air continues to increase until it equals that in the inlet air. The adsorbent is saturated under these operating conditions.[48]

The adsorption of a mixture of adsorbable organic vapors in air is not uniform, and the more easily adsorbed components are those with the higher boiling points. When air containing a mixture of organic vapors is passed over activated carbon, the vapors are equally adsorbed at the start. However, as the amount of the higher boiling component in the adsorbent increases, the more volatile component revaporizes. The exit vapor consists primarily of the more volatile component after the breakpoint has been reached. This process continues for each organic mixture component until the highest boiling component is present in the exit gas. In the control of organic vapor mixtures, the adsorption cycle should be stopped when the first breakpoint occurs as determined by detection of vapors in the exit gas. Many theories have been advanced to explain the selective adsorption of certain vapors or gases. These theories are presented in Perry and Chilton[51] and will not be discussed here.

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[53] Cooper, W. J., et al. Hydrocarbon Pollutant Systems Study; Volume I - Stationary Sources, Effects, and Control. APTD-1499 (PB 219 073), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 20, 1972. 379 pp.

The quantities of organic vapors adsorbed by activated carbon are a function of the particular vapor in question, the adsorbent, the adsorbent temperature, and the vapor concentration. Removal of gaseous vapors by physical adsorption is practical for gases with molecular weights over 45.[51] Each type of activated carbon has its own adsorbent properties for a given vapor, and the quantity of vapor adsorbed for a particular vapor concentration in the gas and at a particular temperature is best determined experimentally. The quantity of vapor adsorbed increases when the vapor concentration increases and the adsorbent temperature decreases.[48]

After breakthrough has occurred, the adsorbent is regenerated by heating the solids until the adsorbate has been removed. A carrier gas must also be used to remove the vapors released. Low pressure saturated steam is used as the heat source for activated carbon and also acts as the carrier gas. Superheated steam at 350°C may be necessary to remove high boiling compounds and return the carbon to its original condition when high boiling compounds have reduced the carbon capacity to the point where complete regeneration is necessary.[52]

Steam requirements for regeneration are a function of external heat losses and the nature of the organic material. The amount of steam adsorbed per kilogram of adsorbate, as a function of elapsed time, passes through a minimum. The carbon should be regenerated for this length of time to permit the minimum use of steam.[51] After regeneration, the carbon is hot and saturated with water. Cooling and drying are done by blowing organic-free air through the carbon bed. Evaporation of the water aids cooling of the carbon. If high temperature steam has been used, other means of cooling the carbon are required.

Fixed-bed adsorbers arrayed in two or more parallel bed arrangements are used to remove organic vapors from air. (See Figure 28.) These are batch-type arrangements where a bed is used until breakthrough occurs and is then regenerated. The simplest adsorber design of this type is a two-bed system where one carbon bed is being regenerated as the other is adsorbing organic vapors. In a three-bed arrangement, a greater quantity of material can be adsorbed per unit of carbon because the effluent passes through two beds in series while the third bed is being regenerated. This

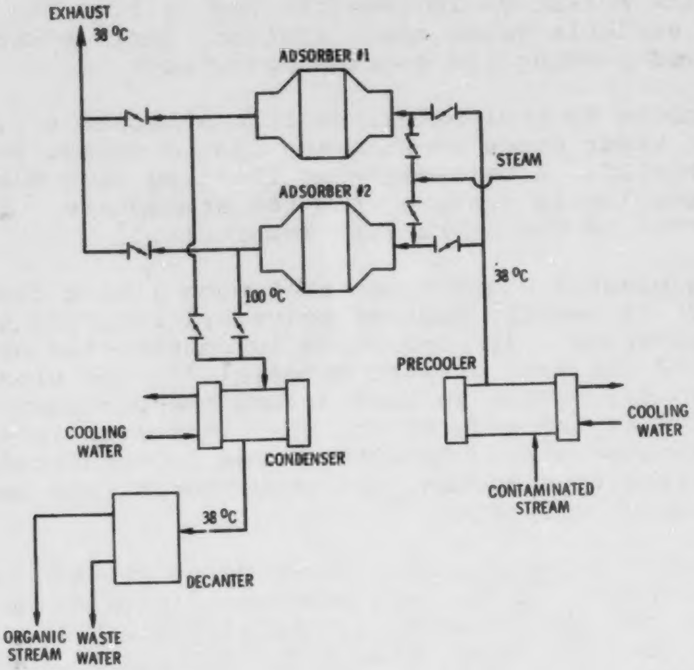
EXHAUST
38 °C
ADSORBER #1
STEAM
ADSORBER #2
38 °C
100 °C
PRECOOLER
COOLING WATER
COOLING WATER
CONDENSER
CONTAMINATED STREAM
38 °C
DECANTER
ORGANIC STREAM
WASTE WATER

Figure 28. Carbon adsorption system.[53]

permits the activated carbon to be used after breakthrough since the second bed in the series removes organic vapors in the exit gas from the first bed. When the first bed is saturated, it is removed from the stream for regeneration; the bed which was used to remove the final traces of organic vapors from the effluent then becomes the new first bed; and the bed which has been regenerated becomes the new second bed.[48]

Heat is released in the adsorption process, which causes the temperature of the adsorbent to increase. If the concentration of organic vapors is not high, as in the case of room ventilators, the temperature rise is typically 10°C.[45,48]

The pressure drop through a carbon bed is a function of the gas velocity, bed depth, and carbon particle size. Activated carbon manufacturers supply empirical correlations for pressure drop in terms of these quantities. These correlations usually include pressure drop resulting from directional change of the gas stream at inlet and outlet.[48]

E. CONTROL OF EMISSIONS FROM STORAGE TANKS

Emissions from storage tanks are controlled to reduce or eliminate atmospheric emissions, reduce or eliminate fire hazards, and prevent loss of valuable products. Techniques used to control storage tank emissions include the use of floating roofs, plastic blankets, variable vapor space systems, various recovery systems, and modified pumping and storage operations.[45]

Floating roofs control emissions from a volatile liquid by eliminating the vapor space so that the liquid cannot evaporate and later be vented. A well-designed floating roof must completely seal off the liquid surface from the atmosphere. The seal for the floating roof is therefore very important.[45]

A floating plastic blanket operates much like a floating roof. The blanket is usually made of polyvinyl chloride but can be made of other plastics. Its underside is constructed of a large number of floats of the same plastic material.[45] The blanket is custom designed to fit within an inch around the periphery. A vertically raised skirt at the edge of the blanket serves as a vapor seal over the annular area. Once this area is saturated with vapor, no further evaporation occurs, and atmospheric loss occurs only through gaseous diffusion.[45]

Variable vapor space systems, designed to contain the vapors produced in storage, can include storage of similar or related products. They use the advantage of inbalance pumping situations where only the tank vapor spaces are manifolded together. The manifold system maintains a balanced pressure drop in all the branches while not exceeding allowable pressure drops. Each tank has an isolating valve so that it can be removed from the vapor balance system during gauging or sampling operations. When vapors exceed the capacity of the balance system, they are incinerated.[45]

The vapor recovery system is very similar yet superior to the vapor balance system. It is more flexible as to the number of tanks and products being stored and can handle vapors from filling operations as well as from tank breathing. Vapors are recovered, compressed, and charged to an absorption unit for recovery of condensable hydrocarbons. Noncondensable vapors are used as fuel or flared.[45]

Fixed-roof tank breathing emissions can be reduced by increasing storage pressure. An increase of 431 Pa (0.063 lbs/sq in.) was found to result in an 8% decrease in emissions due to breathing. Tanks operated at 119 kPa (2 1/2 psig) or higher were found to have little or no breathing emissions. However, the pressure setting must not exceed the weight of the roof. Another method of reducing storage tank emissions is based upon the degree of saturation in the vapor space. A baffle located horizontally below the tank vent, as shown in Figures 29 and 30, directs entering atmospheric air into a stratified layer next to the top of the tank. Being lighter, air remains in the tank top area, minimizing mixing with the vapor phase above the liquid surface. This air is also the first expelled during the outbreathing cycle. This system can reduce surface evaporation as much as 25% to 50%.[45]

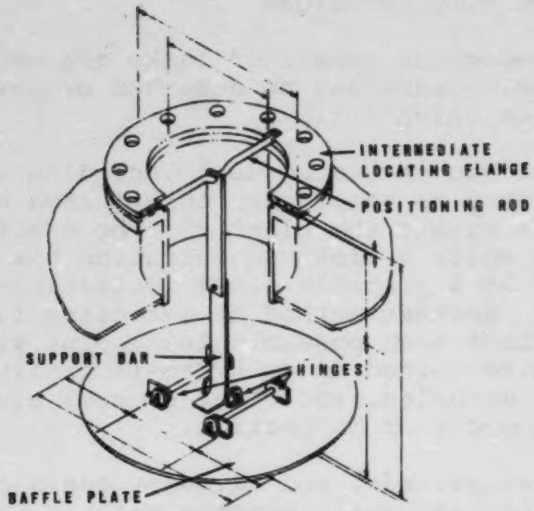
INTERMEDIATE
LOCATING FLANGE
POSITIONING ROD
SUPPORT BAR
HINGES
BAFFLE PLATE

Figure 29. Baffle construction.[45]

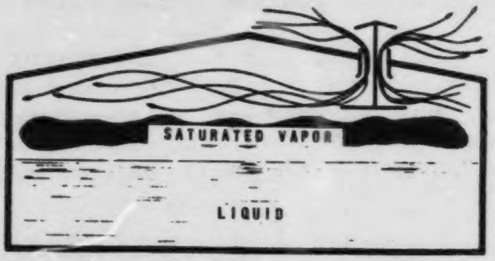
SATURATED VAPOR
LIQUID

Figure 30. Air baffle.[45]

A protective coating of paint applied to the outside shell and roof of a tank can influence vapor space and liquid temperatures. Reflectivity and glossiness of a paint can determine the amount of heat a tank receives via radiation. Breathing emission reductions of 25% for aluminum over black paint and 25% for white over aluminum paint have been reported.[45]

Insulation, spraying water on the roof surface, refrigeration, and autorefrigeration all can reduce heat energy normally conducted to the liquid in the tanks.[45]

Routine operations such as the reading of gauges or sampling can be properly scheduled to minimize emissions from storage tanks. Use of remote level-reading gauges and sampling devices can also reduce emissions.[45]

F. CONTROL OF FUGITIVE EMISSIONS

Rapid detection and quick repair of leaks are necessary to reduce fugitive emissions. Leaks may be detected by several methods, the descriptions of which follow.

A fixed multipoint gas chromatograph, including analyzer and recorder, may be used to sample for chlorinated hydrocarbons periodically at points within the plant.[54] The exact location of the leak in a section where a high concentration has been detected can be determined by a portable flame ionization-type hydrocarbon sensing device.[54] Another method of detecting fugitive leaks is to periodically check each possible leak point with a portable detector.[54] A third method is to hydrostatically test piping, flanges, vessels, manholes, and other process equipment after construction, maintenance, or inspection.[54]

Control of pump, compressor, and agitator seals is provided by the use of double mechanical seals between which a liquid is maintained at a pressure greater than that which exists in the pump, compressor, or agitator. Any leakage that occurs will thus leak into the pump, not out of it.[54] All flanged pipe joints are potential leak sources for which welded connections can be used.

Emissions resulting from sampling for laboratory analysis can be eliminated by letting the gas to be sampled flow through the sample flask to a lower pressure point in the process. The sample flask is then blocked off, and any material that remains in the sample lines can be purged with inert gas to a recovery system or a control device.[54]

During loading and unloading of raw material, byproducts, and products, two hoses are connected to a railroad car or barge. The bottom hose transfers the material while the other, located at the top, maintains pressure. Material left in the hoses may be lost to the atmosphere on disconnection. This can be controlled by purging the lines to a control device with inert gas.[54]

Emissions from pressure relief valves located on all pressure vessels are controlled by a rupture disc installed between the vessel and the safety valve and a pressure gauge installed between the valve and rupture disc.[54] Pressure buildup between the disc and the valve indicates rupture disc failure.

Emissions resulting from excessive pressure are controlled by connecting the relief valve discharge to a flare or another control device. Material present in equipment that is opened for maintenance or inspection can be controlled by purging the equipment with inert gas or displacing the contents with water before opening.[54]

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[54] Evans, L., et al. Standard Support Environmental Impact Document, Volume II. Draft copy of report. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, North Carolina, March 1975.

G. WASTE DISPOSAL TECHNIQUES

Major sources of pollution are the liquid and solid waste materials that are formed during the manufacture of chlorinated hydrocarbons. This waste is generated along with useful products by the side reactions that take place when chlorine or hydrogen chloride is reacted with hydrocarbons.

Until fairly recently, such waste was disposed of by ocean dumping, landfilling, deep welling, open pit burning, lagooning, and conventional incineration. But with increasing quantities of waste being produced and increasing concern over the environment, these relatively cheap disposal options can no longer be regarded as adequate.[55,57] Incineration still remains the best option available.[58,59]

Chlorinated hydrocarbons are very stable compounds, and high temperatures (approximately 1900°C) are required to destroy them. Moreover, at these high temperatures, chlorine and hydrogen chloride are produced,[60,61] and this poses a serious corrosion problem. Conventional incinerators are lined with refractory linings that cannot stand these high temperatures or tolerate the corrosion

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[55] Solving waste problems profitably. Chemical Week, 104(24):38-39, 1969.

[56] Ross, R. D., and C. E. Hulswitt. Safe Disposal of Chlorinated and Fluorinated Waste Materials. For presentation at the 62nd Annual Meeting of the Air Pollution Control Association, New York, New York, June 22-26, 1969. 19 pp.

[57] Hot option for disposal of hydrocarbon wastes. Chemical Week, 110(16):37-38, 1972.

[58] Lewis, C. R., R. E. Edwards, and M. A. Santoro. Incineration of Industrial Wastes at a Large Multi-Product Chemical Plant. For presentation at the National Waste Processing Conference, New York, New York, June 1976. 9 pp.

[59] Dunn, K. S. Incineration's role in ultimate disposal of process wastes. Chemical Engineering, Deskbook Issue, 82(21):141-150, 1975.

[60] Hulswitt, C. E., and J. A. Mraz. HCl Recovered from Chlorinated Organic Waste. Chemical Engineering, 79(10):80-81, 1972.

[61] Monroe, E. S. Combustion, Air Pollution, and Common Sense. In: Proceedings of the First Mid-Atlantic Industrial Waste Conference, University of Delaware, Newark, Delaware, November 13-15, 1967. pp. 215-222.

condition. Combustion at lower temperatures in conventional incinerators is incomplete, which causes a pollution problem. Moreover, highly chlorinated waste will not support combustion in conventional incinerators; it requires high performance burners.[55,62]

Specialized disposal units are required. They must have high performance burners and be lined with corrosion-resistant refractory material capable of withstanding high temperatures. They must also be able to recover chlorine as usable hydrochloric acid or as anhydrous hydrogen chloride.[60] One such unit has been developed jointly by Thermal Research and Engineering Corporation and Union Carbide. The system utilizes the Sub-X Incinerator-Scrubber and the UCAR HCl Recovery System to destroy chlorinated waste produced during the manufacture of chlorinated hydrocarbons.[55,57,60,62,63] The waste disposal system is designed to handle chlorinated hydrocarbon wastes which contain from 20% to 90% chlorine.

A schematic flow diagram for the disposal of chlorinated hydrocarbon wastes is presented in Figure 31. The disposal system is comprised of two sections: incinerator and HCl recovery. Figure 31 shows the processing scheme used to produce either 27% HCl or anhydrous HCl.[60]

1. Incinerator Section (Sub-X Incinerator-Scrubber)

The incinerator section of the disposal system consists of a burner and a quencher. The burner is an air-atomized vortex burner which is capable of atomizing the chlorinated hydrocarbon waste to about 0.04μm. Chlorinated hydrocarbon wastes containing less than 70% chlorine will burn without auxiliary fuel.[60] Wastes containing 20% to 30% chlorine have heating values of 23,300 to 28,000 kJ/kg and are capable of producing 1930°C flame temperatures without auxiliary fuel. From 30% to 70% chlorine, heating values decline to 10,500 to 12,600 kJ/kg, and flame temperatures decline to 1370°C.[62] Auxiliary fuel is required to maintain flame temperatures in the range of 1370°C to 1930°C. Wastes containing more than 70% chlorine will not support combustion alone. In this case, the auxiliary fuel provides:[62]

- Heat required for waste decomposition
- Flame temperature in the 1,370°C to 1,930°C range
- Hydrogen to prevent formation of chlorine

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[62] Santoleri, J. J. Chlorinated Hydrocarbon Waste Disposal and Recovery Systems, Chemical Engineering Progress, 69(1):68-74, 1973.

[63] Finding profits in chlorinated hydrocarbon wastes. Chemical Week, 111(23):39, 1972.

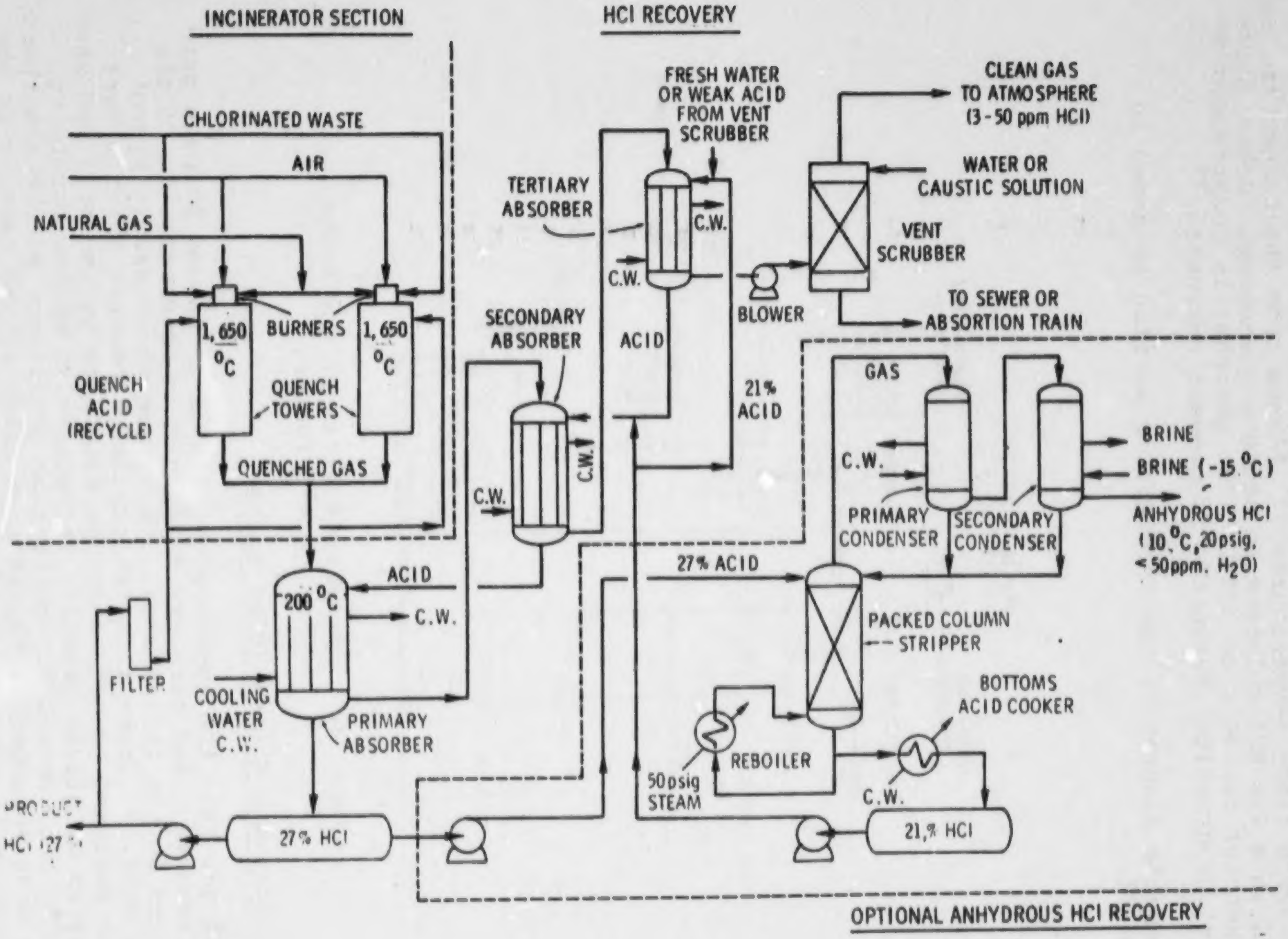
INCINERATOR SECTION
HCl RECOVERY
CHLORINATED WASTE
AIR
NATURAL GAS
BURNERS
1,650 °C
1,650 °C
QUENCH ACID (RECYCLE)
QUENCH TOWERS
QUENCHED GAS
FILTER
200 °C
ACID
C.W.
COOLING WATER C.W.
PRIMARY ABSORBER
PRODUCT HCl (27%)
27% HCl
SECONDARY ABSORBER
C.W.
C.W.
TERTIARY ABSORBER
FRESH WATER OR WEAK ACID FROM VENT SCRUBBER
C.W.
C.W.
ACID
21% ACID
BLOWER
VENT SCRUBBER
CLEAN GAS TO ATMOSPHERE (3-50 ppm HCl)
WATER OR CAUSTIC SOLUTION
TO SEWER OR ABSORTION TRAIN
GAS
C.W.
PRIMARY CONDENSER
SECONDARY CONDENSER
BRINE
BRINE (-15 °C)
ANHYDROUS HCl (10 °C, 20 psig, <50 ppm. H2O)
27% ACID
PACKED COLUMN STRIPPER
REBOILER
50 psig STEAM
BOTTOMS ACID COOKER
C.W.
21% HCl
OPTIONAL ANHYDROUS HCl RECOVERY

Figure 31. Schematic flow diagram for the disposal of chlorinated hydrocarbon wastes.[60]

The quencher used in the incinerator section is unique in design since it must protect the processing equipment from damage from the 1,930°C flame temperatures.[55] Flames from the burner are submerged in a 27% HCl solution to achieve quenching. Gases leave the quencher at 150°C to 370°C. The quencher is constructed of impervious graphite (Karbate®) to prevent corrosion.[55]

A schematic diagram of the incinerator section is shown in Figure 32.

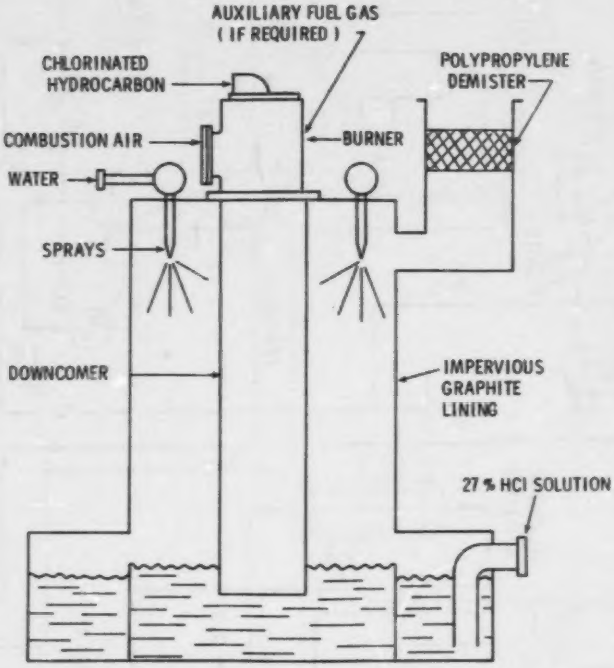
AUXILIARY FUEL GAS
(IF REQUIRED)
CHLORINATED HYDROCARBON
POLYPROPYLENE DEMISTER
COMBUSTION AIR
BURNER
WATER
SPRAYS
DOWNCOMER
IMPERVIOUS GRAPHITE LINING
27% HCl SOLUTION

Figure 32. Schematic diagram of the Sub-X Incinerator-Scrubber.[56]

2. HCl Recovery System (UCAR System)

Quenched gas from the incinerator section is passed through primary, secondary, and tertiary falling film absorbers.[60] Of the HCl formed in the incinerator, 99% is recovered as 27% hydrochloric acid.[60] Gases from the tertiary absorber enter a vent scrubber designed to reduce HCl emissions to 50 ppm or 3 ppm when using water or dilute caustic, respectively, as the scrubbing liquid.[60] The overall HCl collection efficiency of the absorbers and the vent scrubber is 99.96% when using dilute caustic in the vent scrubber.[60]

The 27% hydrochloric acid can be upgraded to anhydrous HCl containing less than 50 ppm H_2O.[60] A conventional packed column stripper is used to convert the 27% hydrochloric acid to 75% to 80% vapors. These vapors are cooled to about 16°C to yield 99% HCl vapors, which are further cooled to -12°C in a brine condenser to reduce water content to 50 ppm.[60]

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. METHYL CHLORIDE

1. Present Technology

In 1975 total U.S. capacity for methyl chloride was estimated to be 2.81×10^5 metric tons per year.[1] This represents 2.45% of all major chlorinated hydrocarbon capacity. Production in 1975 was 1.42×10^5 metric tons.[1] The major producers in the United States are Allied Chemical Corporation, Continental Oil Company, Diamond Shamrock Corporation, Dow Chemical U.S.A., Dow Corning Corporation, Ethyl Corporation, General Electric Company, Stauffer Chemical Company, and Union Carbide. The 9 companies manufacture methyl chloride at 11 locations.[1] Tables 23[1] and 24[1] list the manufacturing companies with their locations and capacities for the chlorination and hydrochlorination processes.

Methyl chloride is domestically produced by two industrial processes: (1) direct chlorination of methane and (2) hydrochlorination of methanol. In 1975 approximately 86% of the industrial capacity was based on hydrochlorination of methanol, while 14% was based on direct chlorination of methane.

2. Industry Production Trends

Historically, growth averaged 5.3% per year between 1965 and 1975 and is expected to be 6% per year through 1980.[1] Figure 33 shows production from 1960 through 1980.[1,64-72]

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[64] Synthetic Organic Chemicals - United States Production and Sales, 1974. ITC Publication 776, United States International Trade Commission, Washington, D.C., 1976. 256 pp.

[65] Synthetic Organic Chemicals - United States Production and Sales, 1973. ITC Publication 728, United States International Trade Commission, Washington, D.C., 1975. 258 pp.

[66] Synthetic Organic Chemicals - United States Production and Sales, 1972. TC Publication 681, United States Tariff Commission, Washington, D.C., 1974. 260 pp.

TABLE 23. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR METHYL CHLORIDE PRODUCTION BY THE CHLORINATION OF METHANE[1]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	31,751
Stauffer Chemical Co.	Louisville, KY	6,804
Total capacity		38,555
Average capacity		19,278
Percent of total methyl chloride capacity		14

TABLE 24. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOT METHYL CHLORIDE PRODUCTION BY THE HYDROCHLORINATION OF METHANOL[1]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Moundsville, WV	11,340
Continental Oil Co.	Lake Charles, LA	45,359
Diamond Shamrock Corp.	Belle, WV	11,340
Dow Chemical U.S.A.	Plaquemine, LA	68,039
Dow Corning	Carrolton, KY	9,072
Dow Corning	Midland, MI	6,804
Ethyl Corp.	Baton Rouge, LA	45,359
General Electric	Waterford, NY	22,680
Union Carbide	Institute, WV	22,680
Total capacity		242,673
Average capacity		26,964
Percent of total methyl chloride capacity		86

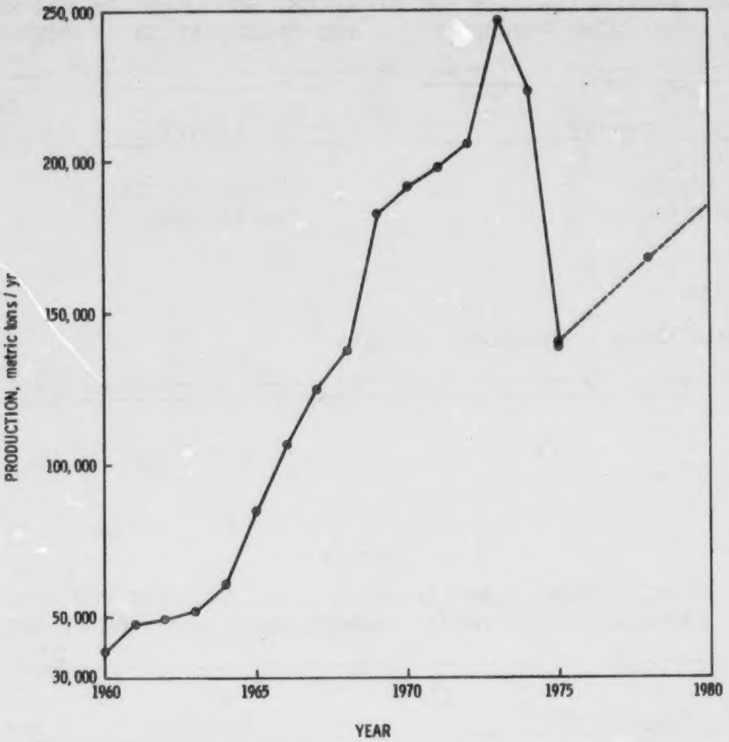

Figure 33. Methyl chloride production, 1960 to 1980.[1,64-72]

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[67] Synthetic Organic Chemicals - United States Production and Sales, 1971. TC Publication 614, United States Tariff Commission, Washington, D.C., 1973. 258 pp.

[68] Synthetic Organic Chemicals - United States Production and Sales, 1969. TC Publication 412, United States Tariff Commission, Washington, D.C., 1971. 251 pp.

[69] Synthetic Organic Chemicals - United States Production and Sales, 1968. TC Publication 327, United States Tariff Commission, Washington, D.C., 1970. 266 pp.

[70] Synthetic Organic Chemicals - United States Production and Sales, 1967. TC Publication 295, United States Tariff Commission, Washington, D.C., 1969. 212 pp.

[71] Synthetic Organic Chemicals - United States Production and Sales, 1966. TC Publication 248, United States Tariff Commission, Washington, D.C., 1968. 214 pp.

[72] Synthetic Organic Chemicals - United States Production and Sales, 1965. TC Publication 206, United States Tariff Commission, Washington, D.C., 1967. 212 pp.

Table 25 gives the uses for methyl chloride.[1]

TABLE 25. METHYL CHLORIDE CONSUMPTION IN 1975[1]

Uses	Percent
Silicones	40
Tetramethyl lead	35
Butyl rubber	4
Methyl cellulose	4
Herbicides	4
Quaternary amines	4
Miscellaneous uses	9
TOTAL	100

Demand for methyl chloride in the silicone industry is likely to increase as new silicone capacity comes onstream in 1977,[1] although recycling of methyl chloride is increasing in that industry. With new cars using unleaded gas, demand for methyl chloride in the manufacture of tetramethyl lead is likely to decrease. Methyl chloride use in herbicides was disappointing as farmers economized by using less or no herbicides.[1]

3. Outlook

Methyl chloride capacity appears to be adequate to supply growing demands for a long time. No new methyl chloride facilities are scheduled, but a small increase in production capacity is possible as one company diverts a portion of its methylene chloride production to methyl chloride.[1]

B. METHYLENE CHLORIDE

1. Present Technology

In 1975 total U.S. capacity for methylene chloride was estimated to be 3.18×10^5 metric tons/yr.[2] This represents 2.8% of all major chlorinated hydrocarbon capacity. Production in 1975 was 2.22×10^5 metric tons (490 million pounds). The major producers in the United States are Allied Chemical Corp., Diamond Shamrock Corp., Dow Chemical U.S.A., Stauffer Chemical Co., and Vulcan Materials Co.[2] The five companies produce methylene chloride at seven locations. Tables 26 and 27 list the manufacturing companies with their locations and capacities for the chlorination and hydrochlorination processes.[2]

Methylene chloride is produced commercially by two processes: (1) direct chlorination of methane and (2) hydrochlorination of methanol. Direct chlorination of methane accounts for 39% of

TABLE 26. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR METHYLENE CHLORIDE PRODUCTION BY THE CHLORINATION OF METHANE[2]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	90,718
Stauffer Chemical Co.	Louisville, KY	27,215
Vulcan Materials Co.	Wichita, KS	6,804
Total capacity		124,737
Average capacity		41,579
Percent of total methylene chloride capacity		39

TABLE 27. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR METHYLENE CHLORIDE PRODUCTION BY THE HYDROCHLORINATION OF METHANOL[2]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Moundsville, WV	22,680
Diamond Shamrock Corp.	Belle, WV	45,359
Dow Chemical U.S.A.	Plaquemine, LA	81,646
Vulcan Materials Co.	Geismar, LA	36,287
Vulcan Materials Co.	Wichita, KS	6,804
Total capacity		192,776
Average capacity		38,555
Percent of total methylene chloride capacity		61

industrial capacity, while the hydrochlorination process accounts for 61%. Methylene chloride capacities are flexible since methylene chloride, methyl chloride, and chloroform are made in the same unit.

2. Industry Production Trends

Historically, growth averaged 13% per year between 1965 and 1975 and is expected to be between 10% and 12% per year through 1980.[2] Figure 34 shows production from 1960 through 1980.

Table 28 summarizes major uses for methylene chloride.[2]

Due to the demise of fluorocarbon propellants and trichloroethylene and since methylene chloride can be easily substituted for fluorocarbons in aerosol applications, growth for methylene

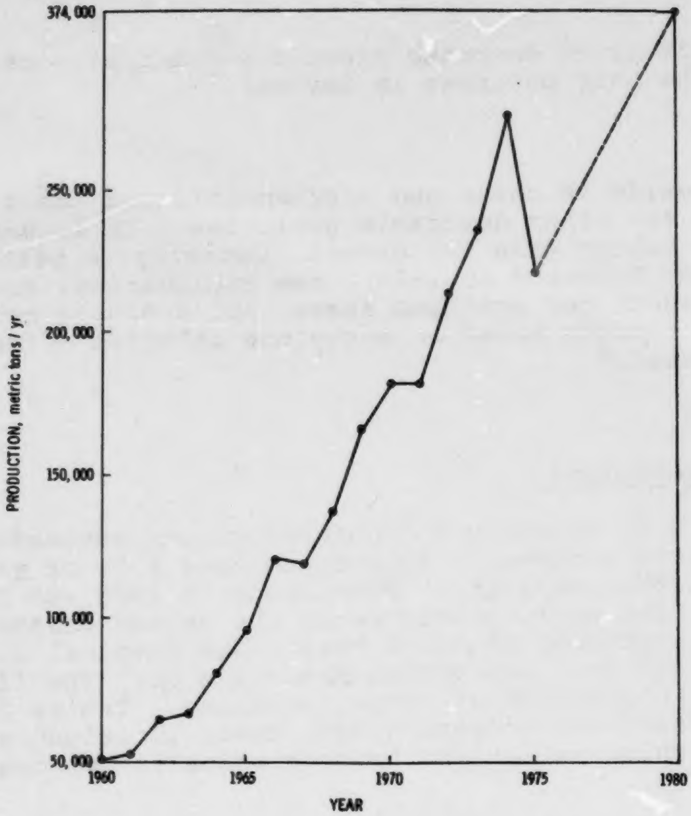

Figure 34. Methylene chloride production, 1960 to 1980.[2,64-72]

TABLE 28. METHYLENE CHLORIDE CONSUMPTION IN 1975[2]

Uses	Percent
Paint remover	30
Aerosols	20
Export	20
Chemical processes, mainly solvent degreasing	10
Plastics	5
Miscellaneous	15
TOTAL	100

chloride is strong in all major end-use areas. Paint removal, vapor degreasing, and adhesive applications all show good, steady growth.[2]

Exports are likely to decrease since Dow Chemical recently has put a chloromethane unit onstream in Germany.[2]

3. Outlook

Methylene chloride is cheap and nonflammable and has a clean health record and other desirable qualities. It is very likely to maintain a better than 10% growth. Capacity is being increased to meet demands expected in 1980. New application, such as use as a blowing agent for urethane foams, and a single operation phosphatizing process based on methylene chloride offer even greater potential.[2]

C. CHLOROFORM

1. Present Technology

In 1975 total U.S. capacity for chloroform was estimated to be 1.95×10^5 metric tons/yr.[3] This represents 1.7% of all major chlorinated hydrocarbon capacity. Production in 1975 was 1.27×10^5 metric tons.[3] The major producers in the United States are Allied Chemical Corp., Diamond Shamrock Corp., Dow Chemical U.S.A., Stauffer Chemical Co., and Vulcan Materials Co. The five companies produce chloroform at seven locations. Tables 29 and 30 list the manufacturing companies with their locations and capacities for the chlorination and hydrochlorination processes, respectively.[3]

TABLE 29. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR CHLOROFORM PRODUCTION BY THE CHLORINATION OF METHANE[3]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	77,110
Stauffer Chemical Co.	Louisville, KY	34,019
Vulcan Materials Co.	Wichita, KS	9,072
Total capacity		120,201
Average capacity		40,067
Percent of total chloroform capacity		61

TABLE 30. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR CHLOROFORM PRODUCTION BY THE HYDROCHLORINATION OF METHANOL.[3]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Moundsville, WV	13,608
Diamond Shamrock Corp.	Belle, WV	18,144
Dow Chemical U.S.A.	Plaquemine, LA	13,608
Vulcan Materials Co.	Geismar, LA	20,865
Vulcan Materials co.	Wichita, KS	9,072
Total capacity		75,297
Average capacity		15,059
Percent of total chloroform capacity		39

Chloroform is made commercially by two processes: (1) direct chlorination of methane and (2) hydrochlorination of methanol. Direct chlorination of methane accounts for approximately 61% of industrial capacity, while hydrochlorination accounts for 39%.

Chloroform, methyl chloride, and methylene chloride are usually produced in the same unit; hence, most capacities are flexible.

2. Industry Production Trends

Historically, growth averaged 9.2% per year between 1965 and 1975 and is expected to range between 8% and 10% per year through 1980.[3] Figure 35 shows production from 1960 through 1980.

Table 31 gives the major uses for chloroform.[3]

Currently, demand has been exceptionally strong, running close to capacity for some producers. Barring complications from the fluorocarbon controversy, growth in the two major end-used areas should continue. The ozone depletion effect of fluorocarbons has considerable effect on the future growth of chloroform. An across-the-board ban on fluorocarbons would significantly affect chloroform production.[3]

3. Outlook

Currently the National Academy of Science is completing a study on fluorocarbons and their effect on the ozone layer, with the report due within 2 years. Chloroform growth will depend on the results of this study. Newer fluorocarbons (fluoropolymers) have proven to be viable for various end uses and should show good growth through 1980. New capacity which will soon come onstream will ease some of the recent pressure felt (1975).[3]

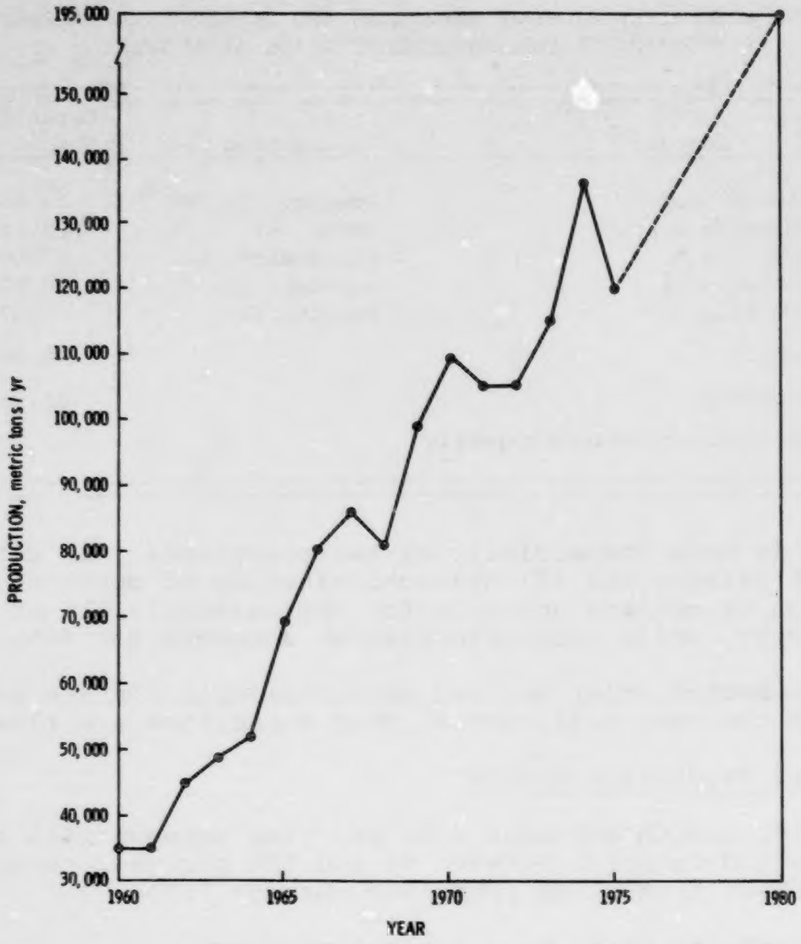

Figure 35. Chloroform production, 1960 to 1980.[3,64-72]

TABLE 31. CHLOROFORM CONSUMPTION IN 1975[3]

Use	Percent
Fluorocarbon refrigerants and propellants	60
Fluorocarbon plastics	30
Export and miscellaneous	10
TOTAL	100

D. CARBON TETRACHLORIDE

1. Present Technology

In 1975 total U.S. capacity for carbon tetrachloride was estimated to be 7.63×10^5 metric tons/yr. This represents 6.7% of all major chlorinated hydrocarbon capacity. Production in 1975 was 4.8×10^5 metric tons.[4] The major producers in the United States are Allied Chemical Corp., Dow Chemical U.S.A., E. I. duPont de Nemours and Co., Inc., FMC Corp., Stauffer Chemical Co., and Vulcan Materials Co. The 6 companies produce carbon tetrachloride at 11 locations. Carbon tetrachloride is made by three industrial processes: (1) direct chlorination of methane, (2) direct chlorination of carbon disulfide, and (3) direct chlorination of propane. Direct chlorination of methane accounts for 55% of the carbon tetrachloride manufactured. Direct chlorination of carbon disulfide is the oldest of the three methods and accounts for 30% of industrial capacity. Direct chlorination of propane accounts for the remaining 15% of carbon tetrachloride industrial capacity. Tables 32, 33, and 34 list the manufacturing companies with their locations and capacities for the three industrial processes currently used.[4]

TABLE 32. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR CARBON TETRACHLORIDE PRODUCTION BY THE CHLORINATION OF METHANE[4]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Moundsville, WV	3,629
Dow Chemical U.S.A.	Freeport, TX	61,235
Dow Chemical U.S.A.	Pittsburg, CA	18,144
E. I. du Pont de Nemours	Corpus Christi, TX	226,795
FMC Corporation	South Charleston, WV	68,039
Stauffer Chemical Co.	Louisville, KY	7,938
Vulcan Materials Co.	Geismar, LA	20,412
Vulcan Materials Co.	Wichita, KS	13,608
Total capacity		419,800
Average capacity		52,475
Percent of total carbon tetrachloride capacity		55

TABLE 33. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR CARBON TETRACHLORIDE PRODUCTION BY THE CHLORINATION OF CARBON DISULFIDE[4]

Company	Location	Capacity, metric tons/yr
FMC Corporation	South Charleston, WV	68,039
Stauffer Chemical Co.	Le Moyne, AL	90,718
Stauffer Chemical Co.	Niagara Falls, NY	68,039
Total capacity		226,796
Average capacity		75,598
Percent of total carbon tetrachloride capacity		30

TABLE 34. MANUFACTURER, PLANT LOCATION, AND CAPACITY FOR CARBON TETRACHLORIDE PRODUCTION BY THE CHLORINATION OF PROPANE[4]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Pittsburg, CA	18,144
Dow Chemical U.S.A.	Plaquemine, LA	56,699
Stauffer Chemical Co.	Louisville, KY	7,938
Vulcan Materials Co.	Geismar, LA	20,412
Vulcan Materials Co.	Wichita, KS	13,608
Total capacity		116,801
Average capacity		23,360
Percent of total carbon tetrachloride capacity		15

2. Industry Production Trends

Historically, growth averaged 6.8% per year between 1964 and 1974 and is expected to decline at an average rate of approximately 10% per year through 1979.[4] Figure 36 shows production from 1960 through 1980.

Table 35 gives the uses for carbon tetrachloride.[4]

TABLE 35. CARBON TETRACHLORIDE CONSUMPTION IN 1975[4]

Use	Percent
Fluorocarbons 11 and 12 (trichlorofluoromethane and dichlorodifluoromethane	95
Other	5
TOTAL	100

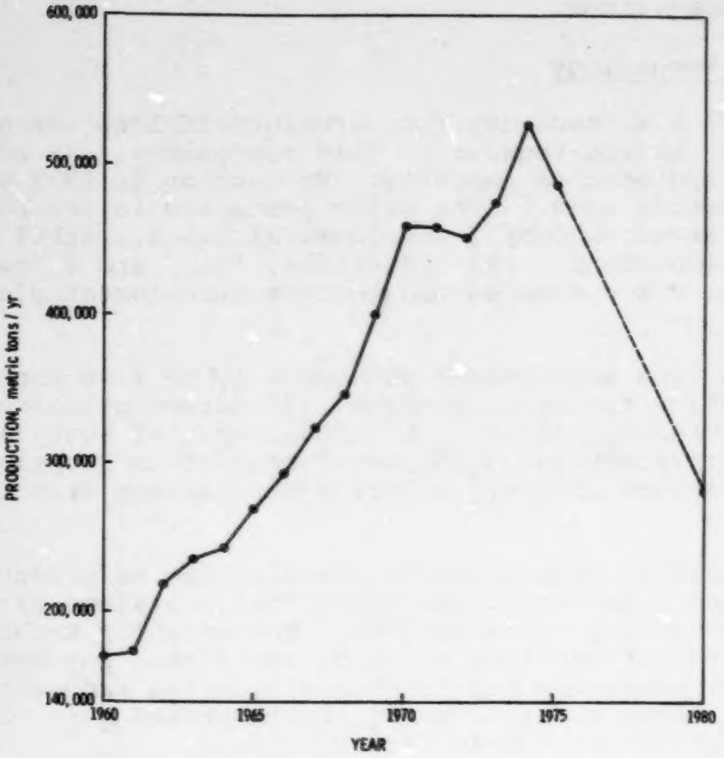

Figure 36. Carbon tetrachloride production, 1960 to 1980.[4,64-72]

Fluorocarbons 11 and 12 are used primarily to manufacture aerosols. Total fillings of aerosol and pressurized products dropped 5% in 1974. The causes were economic plus the issue of ozone depletion by fluorocarbons. Health controversies surrounding fluorocarbon propellants will permanently decrease demand for aerosols even if fluorocarbons do not cause ozone depletion. This has a very negative effect on the production of carbon tetrachloride, which is expected to decrease.[4]

3. Outlook

If the National Academy of Science report on fluorocarbons confirms that these materials destroy the stratospheric ozone layer, close to one-half of the carbon tetrachloride market will be closed.[4]

E. PERCHLOROETHYLENE

1. Present Technology

In 1975 total U.S. capacity for perchloroethylene was estimated to be 5.01 x 10^5 metric tons/yr.[5] This represents 4.4% of all major chlorinated hydrocarbon capacity. Production in 1975 was 3.16 x 10^5 metric tons.[5] The major producers in the United States are Diamond Shamrock Corp., Dow Chemical U.S.A., Ethyl Corp., Occidental Petroleum Corp., PPG Industries, Inc., and Vulcan Materials Co. The six companies manufacture perchloroethylene at nine locations.[5]

Perchloroethylene is produced commercially by five processes: (1) direct chlorination of propane, (2) direct chlorination of ethylene dichloride, (3) direct chlorination of acetylene, (4) as a byproduct of propylene oxide manufacture from propylene, and (5) as a byproduct of vinyl chloride manufacture from ethylene dichloride.

It is difficult to determine the distribution of production of perchloroethylene from feedstocks other than acetylene since many companies use a variety of feedstocks. The original method for producing perchloroethylene was from acetylene, but because of expensive raw materials and expensive chlorine recovery from hydrochloric acid, this route is being slowly phased out. Currently 3% of perchloroethylene is made from acetylene.

Chlorination of ethylene dichloride represents 35% of industrial capacity. The major process for making perchloroethylene is by chlorination of propane, and it is estimated that this utilizes 44% of industrial capacity.

Table 36 lists the three manufacturing companies, with their locations and capacities, that manufacture perchloroethylene by the chlorination of propane process.[5]

2. Industry Production Trends

Historically, growth averaged 6% per year between 1965 and 1975 and is expected to range between 3% and 4% per year through 1980.[5] Figure 37 shows production from 1960 through 1980.

Table 37 gives the major uses for perchloroethylene.[5]

Perchloroethylene growth has been improving in degreasing and chemical intermediate uses. Being an exempt solvent, perchloroethylene is in demand.[5] However, the domestic drycleaning market is declining, and the psychological fallout from the fluorocarbon controversy has hurt intermediate use.[5]

TABLE 36. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR PERCHLOROETHYLENE PRODUCTION BY THE CHLORINATION OF PROPANE[5]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	54,431
Dow Chemical U.S.A.	Pittsburg, CA	9,072
Dow Chemical U.S.A.	Plaquemine, LA	68,039
Vulcan Materials Co.	Geismar, LA	68,039
Vulcan Materials Co.	Wichita, KS	22,680
Total capacity		222,261
Average capacity		44,452
Percent of total perchloroethylene capacity		44

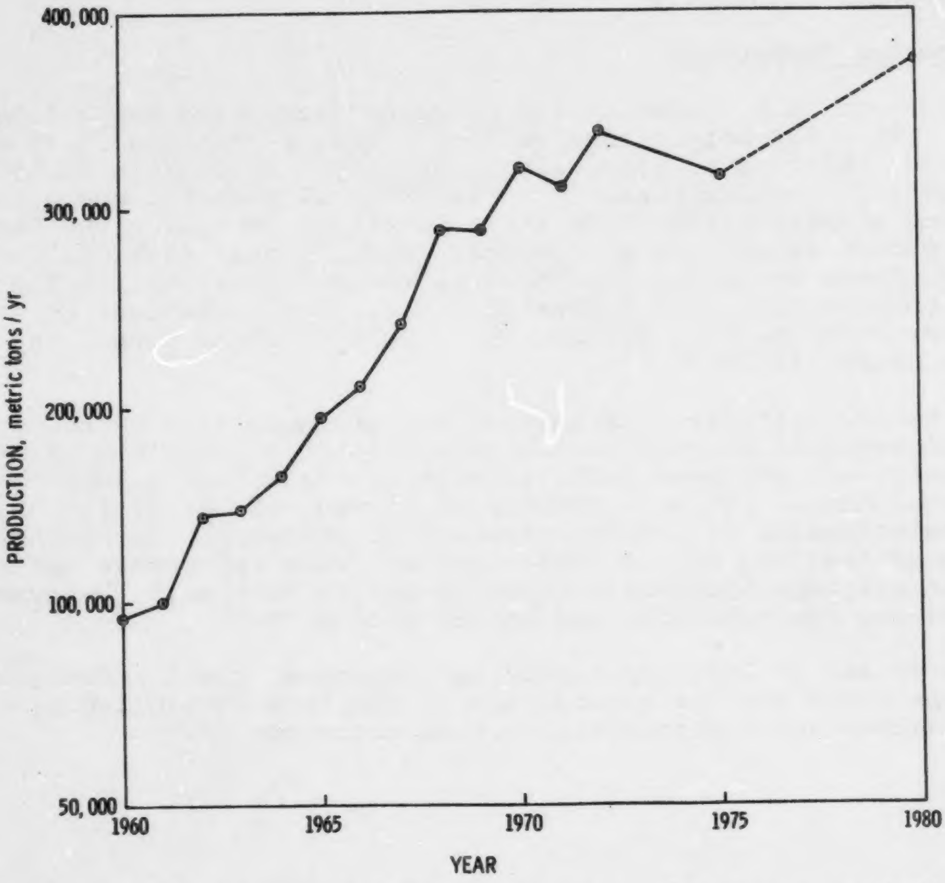

Figure 37. Perchloroethylene production, 1960 to 1980.[5,64-72]

TABLE 37. PERCHLOROETHYLENE CONSUMPTION IN 1975[5]

Use	Percent
Drycleaning solvent	63
Industrial metal cleaning	14
Chemical intermediate (mostly fluorocarbons)	13
Export and miscellaneous	10
TOTAL	100

3. Outlook

EPA's regulatory pressure on other solvents will continue to increase perchloroethylene's market share somewhat. However, barring new uses, growth cannot be expected to exceed 4% annually.[5]

F. ETHYLENE DICHLORIDE

1. Present Technology

In 1975 total U.S. capacity for ethylene dichloride was estimated to be 5.89×10^6 metric tons/yr.[24,31] This represents 51.4% of all major chlorinated hydrocarbon capacity. Production in 1975 was 5.0×10^6 metric tons.[24,31] In 1975, 12 chemical companies produced ethylene dichloride at 17 locations in the United States. Major producers are Allied Chemical Corp., Continental Oil Co., Diamond Shamrock Corp., Dow Chemical U.S.A., Ethyl Corp., The B. F. Goodrich Co., PPG Industries, Inc., Shell Chemical Co., Stauffer Chemical Co., Texaco, Inc., Union Carbide Corp., and Vulcan Materials Co.[24,31]

Prior to 1970, ethylene dichloride was produced as a byproduct in the chlorohydrin process for the manufacture of ethylene oxide. Currently, all ethylene oxide is made by the direct oxidation of ethylene; hence, ethylene dichloride is made either by the oxyhydrochlorination or the chlorination of ethylene. It has been estimated that the oxyhydrochlorination route represents 52% of current ethylene dichloride capacity and is increasing because of its cheaper raw materials and higher yields.[24,31]

Tables 38 and 39 list manufacturing companies, plant locations, and capacities for the manufacture of ethylene dichloride by the chlorination and oxyhydrochlorination processes.[24,31]

2. Industry Production Trends

Historically, growth averaged 9% per year from 1969 through 1974 and is expected to be 4% per year through 1979. Figure 38 shows production capacity of ethylene dichloride from 1960 through 1980.[24,31,64-72]

TABLE 38. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR ETHYLENE DICHLORIDE PRODUCTION BY THE CHLORINATION OF ETHYLENE[24,31]

Company	Location	Capacity, metric tons/yr
Continental Oil Co.	Westlake, LA	523,900
Dow Chemical Co.	Oyster Creek, TX	498,950
Dow Chemical Co.	Plaquemine, LA	601,010
Ethyl Corp.	Baton Rouge, LA	317,510
Ethyl Corp.	Pasadena, TX	117,930
PPG Industries	Lake Charles, LA	544,310
Vulcan Materials Co.	Geismer, LA	149,680
Union Carbide Corp.	Texas City, TX	68,040
Total capacity		2,821,330
Average capacity		352,670
Percent of total ethylene dichloride capacity		48

TABLE 39. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR ETHYLENE DICHLORIDE PRODUCTION BY THE OXYHYDROCHLORINATION OF ETHYLENE[24,31]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Baton Rouge, LA	319,300
Diamond Shamrock Corp.	Deer Park, TX	202,100[a]
Dow Chemical U.S.A.	Freeport, TX	735,000
B. F. Goodrich	Calvert City, KY	459,400[a]
Shell Chemical Co.	Deer Park, TX	551,300[a]
Shell Chemical Co.	Norco, LA	535,200[a]
Stauffer Chemical Co.	Carson, CA	156,200[a]
Texaco, Inc.	Port Neches, TX	32,200
Union Carbide Corp.	Taft, LA	68,900
Total capacity		3,059,600
Average capacity		339,956
Percent of total ethylene dichloride capacity		52

[a] Estimated figures.

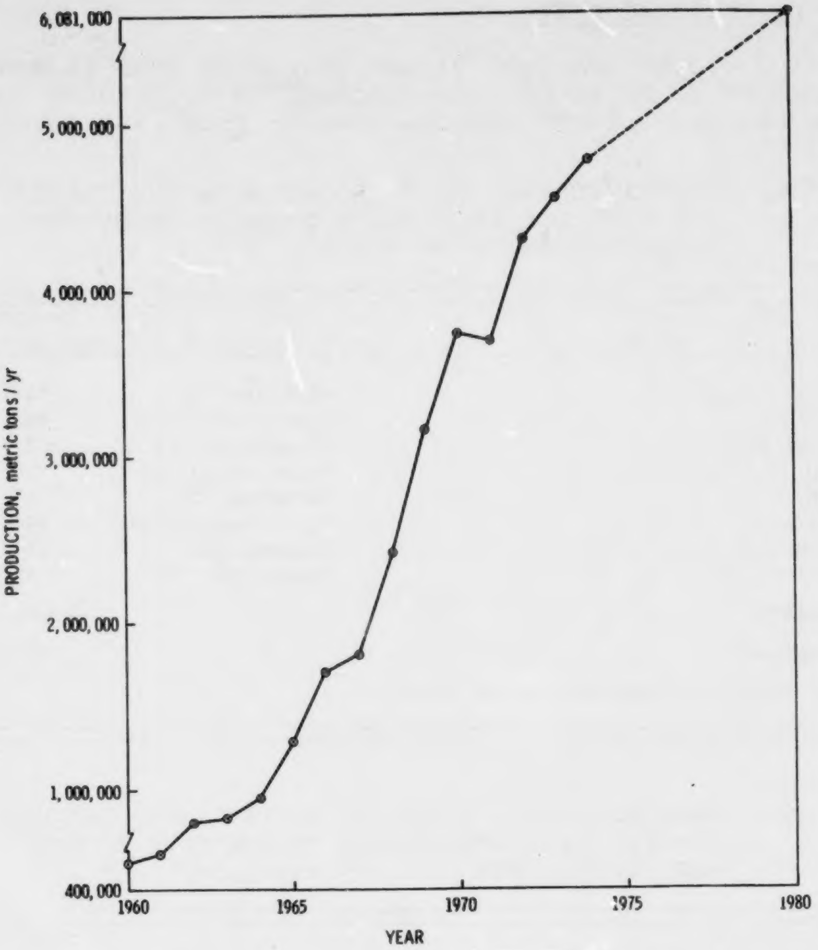

Figure 38. Ethylene dichloride production, 1960 to 1980.[24,31,64-72]

Table 40 summarizes the data for ethylene dichloride uses.[24,31]

Demand for ethylene dichloride to produce vinyl chloride, its major end use, has been increasing steadily at 10% per year. Ethylene dichloride end use to make 1,1,1-trichloroethane, perchloroethylene, vinylidene chloride, and ethylenediamine has grown steadily. Due to EPA regulations, production of trichloroethylene and lead scavengers has declined.[24,31]

3. Outlook

No capacity increases for ethylene dichloride have been announced. With only 76% capacity utilized, there is sufficient capacity onstream to meet the projected 4% increase in demand.

TABLE 40. ETHYLENE DICHLORIDE CONSUMPTION IN 1975[24,31]

Uses	Percent
Vinyl chloride	81
1,1,1-Trichloroethane	3
Trichloroethylene	3
Perchloroethylene	3
Vinylidene chloride	3
Ethyleneamines	3
Lead scavenger	2
Exports	2
Miscellaneous	Negligible
TOTAL	100

Vinyl chloride will continue to be the largest end use for ethylene dichloride. Air pollution control regulations have limited trichloroethylene production. However, its substitutes, 1,1,1-trichloroethane and perchloroethylene, are also ethylene dichloride derivatives so essentially the ban on trichloroethylene use will not affect ethylene dichloride total consumption.

Vinylidene chloride and ethyleneamine consumption and, consequently, ethylene dichloride consumption are expected to increase 7% and 5% per year, respectively, through 1979.

Conversion from leaded to unleaded gas could make ethylene dichloride available for other uses.

G. PHOSGENE

1. Present Technology

In 1975 total U.S. capacity for phosgene was estimated to be 7.22×10^5 metric tons/yr.[6] This represents 6.3% of all major chlorinated hydrocarbon capacity. The production in 1975 was 4.41×10^5 metric tons.[6] The major producers in the United States are Allied Chemical Corp., BASF Wyandotte Corp., Chemetron Corp., E. I. du Pont de Nemours and Co., FMC Corp., General Electric, Jefferson Chemical Co., Mobay Chemical Co., Olin Corp., PPG Industries, Inc., Rubicon Corp., Stauffer Chemical Co., Story Chemical Corp., Union Carbide Corp., The Upjohn Co., and Van De Mark Chemical Co., Inc. These 16 companies produce phosgene at 18 locations.[6] Phosgene is manufactured by the chlorination of carbon monoxide, and its major use (approximately 85%) is in the manufacture of isocyanates.

Table 41 lists manufacturing companies, plant locations, and capacities for the manufacture of phosgene.[6]

TABLE 41. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR PHOSGENE PRODUCTION BY THE CHLORINATION OF CARBON MONOXIDE[6]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Moundsville, WV	44,452
BASF Wyandotte Corp.	Geismar, LA	24,947
Chemetron Corp.	LaPorte, TX	36,287
E. I. du Pont de Nemours Co., Inc.	Deepwater Point, NJ	61,235
FMC Corp.	Baltimore, MD	2,722
General Electric Co.	Mount Vernon, IN	27,215
Mobay Chemical Co.	Baytown, TX	58,967
Mobay Chemical Co.	New Martinsville, WV	111,130
Olin Corp.	Lake Charles, LA	54,431
Olin Corp.	Ashtabula, OH	22,680
PPG Industries	Barberton, OH	2,268
Rubicon Chemicals	Geismar, LA	56,699
Stauffer Chemical Co.	Cold Creek, AL	11,340
Story Chemical Corp.	Muskegon, MI	4,536
Tenaco, Inc.	Port Neches, TX	13,608
Union Carbide Corp.	South Charleston, WV	49,895
The Upjohn Co.	LaPorte, TX	136,077
Van De Mark Chemical Co.	Lockport, NY	3,629
Total capacity		722,118
Average capacity		40,118
Percent of total phosgene capacity		100

2. Industry Production Trends

Historically, growth averaged 15.9% per year between 1963 and 1973 and is expected to be 12% per year through 1980.[6] Figure 39 shows actual and estimated production from 1965 through 1980.[6,64-72]

Table 42 gives the major uses of phosgene.[6]

The growth rate of phosgene closely parallels that of the isocyanates used in urethanes. A strong demand for phosgene-based pesticides has initiated an expansion of nonisocyanate phosgene production.[6] Shortages of chlorine and its high prices when available have created problems in phosgene production.[6]

3. Outlook

Strong growth potential for polycarbonates, pesticides, and isocyanates indicates a continued strong growth for phosgene.[6]

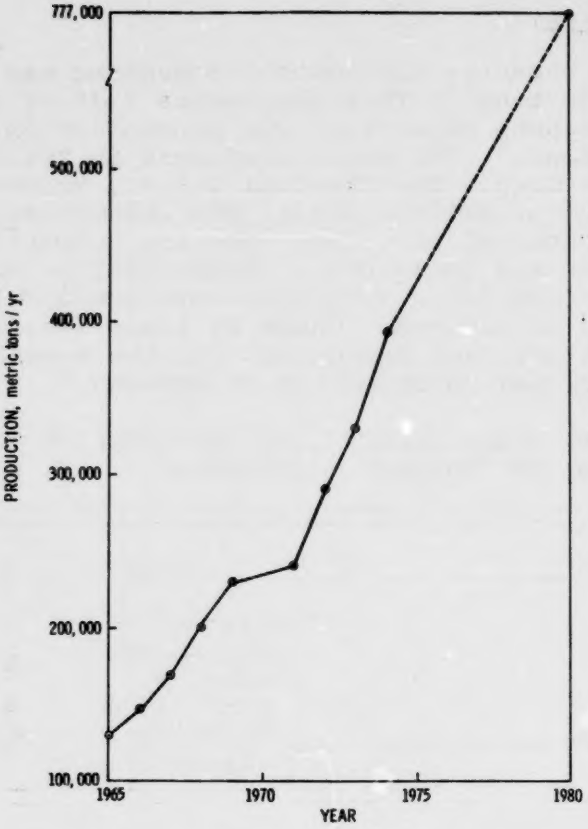

Figure 39. Phosgene production, 1965 to 1980.[6,64-72]

TABLE 42. PHOSGENE CONSUMPTION IN 1975[6]

Use	Percent
Toluene diisocyanate	62
Other (polymeric) isocyanates	23
Polycarbonates	6
Pesticides, carbonates, and specialties	9
TOTAL	100

H. MONOCHLOROBENZENE

1. Present Technology

In 1975 total U.S. capacity for monochlorobenzene was estimated to be 3.13×10^5 metric tons.[7] This represents 2.7% of all major chlorinated hydrocarbons capacity. The production in 1975 was 1.76×10^5 metric tons.[7] The major producers in the United States are Allied Chemical Corp., Dow Chemical U.S.A., Monsanto Co., Montrose Chemical Corp. of California, PPG Industries, Inc., and Standard Chlorine Chemical Co., Inc. The six companies produce monochlorobenzene at six locations.[7] Commercially, monochlorobenzene is manufactured along with *ortho-* and *para*-dichlorobenzene by the chlorination of benzene. Table 43 lists manufacturing companies, plant locations, and capacities for the manufacture of monochlorobenzene by the chlorination of benzene.[7]

TABLE 43. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR MONOCHLOROBENZENE PRODUCTION BY THE CHLORINATION OF BENZENE[7]

Company	Location	Capacity, metric tons/yr
Allied Chemical Corp.	Syracuse, NY	23,587
Dow Chemical U.S.A.	Midland, MI	136,077
Monsanto Co.	Sauget, IL	52,163
Montrose Co.	Henderson, NV	31,751
PPG Corp.	New Martinsville, WV	31,751
Standard Chlorine Co.	Delaware City, DE	34,019
Total capacity		309,348
Average capacity		51,558
Percent of total monochlorobenzene capacity		100

2. Industry Production Trends

Historically, the production declined at an average rate of 2% per year between 1963 and 1973 and is expected to grow at 2% per year through 1978.[7] Figure 40 shows actual and estimated production of monochlorobenzene between 1965 and 1980.

Table 44 gives the major uses for monochlorobenzene.[7]

ortho- and *para*-Nitrochlorobenzene use has been increasing modestly. The demand for DDT to control malaria in foreign countries is expected also to increase dramatically, to nearly double current annual use, by 1982.[7] Use of monochlorobenzene to make phenol is decreasing.

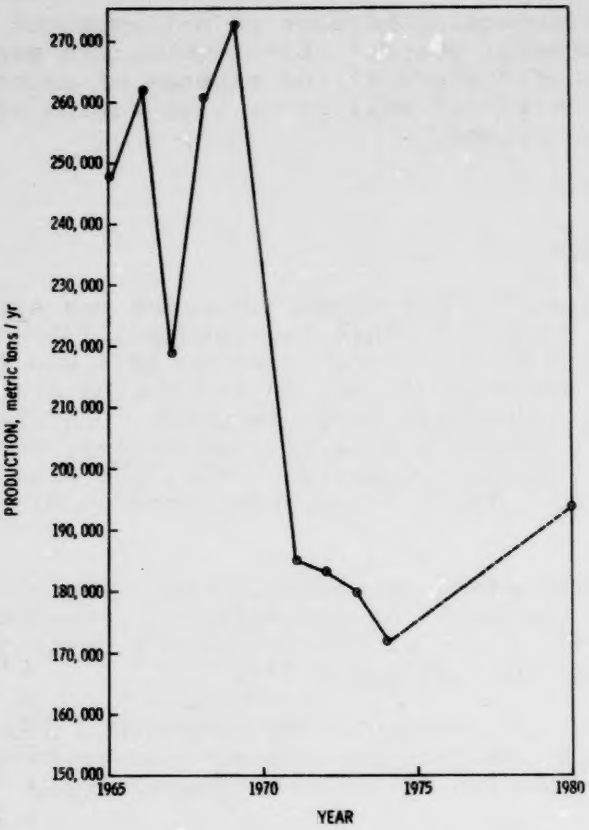

Figure 40. Monochlorobenzene production, 1965 to 1980.[7,64-72]

TABLE 44. MONOCHLOROBENZENE CONSUMPTION IN 1975[7]

Use	Percent
ortho- and *para*-Nitrochlorobenzene	50
Solvent	20
Phenol	10
Miscellaneous	20
TOTAL	100

3. Outlook

Actual production of monochlorobenzene is not expected to increase much over the next several years.[7] Dichlorobenzene manufacture is being stressed by manufacturers at the expense of monochlorobenzene, and newer facilities will favor high ratios of dichlorobenzene to monochlorobenzene.[7]

I. DICHLOROBENZENES

1. Present Technology

In 1975 total U.S. capacity for dichlorobenzene was estimated to be 1.34×10^5 metric tons.[8,9] This represents 1.17% of all chlorinated hydrocarbon capacity. Production in 1975 was 6.58×10^4 metric tons.[8,9] The major producers in the United States are: Allied Chemical Corp., Chemical Products Corp., Dow Chemical U.S.A., ICC Industries, Inc., Monsanto Co., PPG Industries, Inc., Solvent Chemical Co., Inc., Specialty Organics, Inc., and Standard Chlorine Chemical Co., Inc. These 9 companies produce dichlorobenzene at 11 locations.[8,9]

Commercially, dichlorobenzene is manufactured along with monochlorobenzene by the chlorination of benzene. *ortho*-Dichlorobenzene represents 46% of the dichlorobenzene industrial capacity while *para*-dichlorobenzene represents 54%.

Tables 45 and 46 list the manufacturing companies, plant locations, and capacities for the manufacture of *para*- and *ortho*-dichlorobenzenes by the chlorination of benzene, respectively.[8,9]

TABLE 45. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR *p*-DICHLOROBENZENE PRODUCTION BY THE CHLORINATION OF BENZENE[8]

Company	Location	Capacity, metric tons/yr
Allied Chemical Co.	Syracuse, NY	3,629
Dow Chemical U.S.A.	Midland, MI	13,608
Monsanto Co.	Sauget, IL	5,443
PPG Corp.	New Martinsville, WV	9,525
Solvent Chemical Co.	Niagara Falls, NY	4,536
Standard Chlorine Co.	Delaware City, DE	34,019
Specialty Organics	Irwindale, CA	907
Total capacity		71,667
Average capacity		10,238
Percent of total *p*-dichlorobenzene capacity		100

TABLE 46. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR *o*-DICHLOROBENZENE PRODUCTION BY THE CHLORINATION OF BENZENE[9]

Company	Location	Capacity, metric tons/yr
Allied Chemical Co.	Syracuse, NY	3,629
Dow Chemical U.S.A.	Midland, MI	13,608
Monsanto Co.	Sauget, IL	7,257
PPG Corp.	New Martinsville, WV	9,072
Solvent Chemical Co.	Niagara Falls, NY	4,536
Standard Chlorine Co.	Delaware City, DE	22,680
Specialty Organics	Irwindale, CA	907
Total capacity		61,689
Average capacity		8,813
Percent of total *o*-dichlorobenzene capacity		100

2. Industry Production Trends

a. *para*-Dichlorobenzene--

Historically, growth averaged 0.4% per year between 1965 and 1975 and is expected to decline at a rate of 1% per year through 1980.[8] Figure 41 shows actual and predicted production for *p*-dichlorobenzene between 1965 and 1980.[8,9,64-72] Figure 42 shows production for total dichlorobenzenes.[8,9,64-72] Table 47 gives the major uses of *p*-dichlorobenzene.[8]

b. *ortho*-Dichlorobenzene--

Historically, growth averaged 9% per year between 1965 and 1975 and is expected to be 8% per year through 1980.[9] Figure 41 shows actual and predicted production for *o*-dichlorobenzene. Table 48 gives the major uses for *o*-dichlorobenzene.[9]

High-purity *ortho*-dichlorobenzene occupies a strong position in the synthesis of organic pesticides.[9] In the chlorination of benzene, considerable progress has been made in reducing the ratio of *para*- to *ortho*-dichlorobenzene.[9] *ortho*-Dichlorobenzene is the more desirable product, and *para*-dichlorobenzene can be regarded as an occasionally troublesome byproduct.[9]

Higher prices for both benzene and chlorine have resulted in higher prices for the dichlorobenzenes.[8,9]

3. Outlook

There are no new outlets in sight for *para*-dichlorobenzene. Current markets are expected to survive but not to grow over the next five years.[8,9] Government regulations for chlorinated benzenes

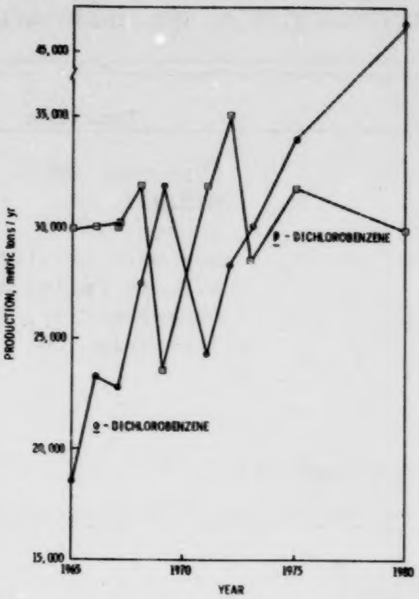

Figure 41. *p*-Dichlorobenzene and *o*-dichlorobenzene production, 1965 to 1980.[8,9,64-72]

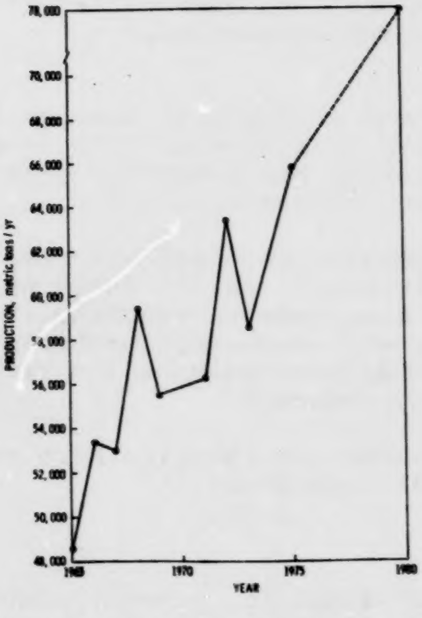

Figure 42. Dichlorobenzene production, 1965 to 1980.[8,9,64-72]

TABLE 47. *p*-DICHLOROBENZENE CONSUMPTION IN 1975[8]

Use	Percent
Space odorant	50
Moth control	40
Other	10
TOTAL	100

TABLE 48. *o*-DICHLOROBENZENE CONSUMPTION IN 1975[9]

Use	Percent
Organic synthesis (chiefly as pesticide intermediate)	65
Toluene diisocyanate process solvent	15
Miscellaneous solvent uses	10
Dyestuff manufacture	5
Other	5
TOTAL	100

will continue to have an impact on solvent use of *ortho*-dichlorobenzene. Growth will follow the long-term agricultural chemical outlook and capacity should be adequate.[8,9] As demand for *ortho*-dichlorobenzene and its production increases, so will the *para*-dichloro-benzene output.[8,9]

J. ETHYL CHLORIDE

1. Present Technology

In 1975 total U.S. capacity for ethyl chloride was 4.65×10^5 metric tons/yr.[11] This represents 3.4% of all major chlorinated hydrocarbon capacity. The production in 1975 was 2.61×10^5 metric tons.[11] The major producers in the United States are Dow Chemical U.S.A., E. I. du Pont de Nemours and Co., Inc., Ethyl Corp., PPG Industries, Inc., Shell Chemical Co., and Stauffer Chemical Co.[11] These six companies produce ethyl chloride at seven locations.

Ethyl chloride is manufactured industrially by two chemical processes: (1) chlorination of ethane and (2) hydrochlorination of ethylene. Currently, chlorination of ethane accounts for approximately 17% of the ethyl chloride industrial capacity, and hydrochlorination of ethylene accounts for the remaining 83%. The plant capacity directed toward the production of ethyl chloride by the chlorination of ethane is not distinguished from the total industry capacity. For the purposes of this report, all the ethyl chloride was assumed to be produced by hydrochlorination.

Table 49 lists the manufacturing companies, plant locations, and capacities for the manufacture of ethyl chloride by the hydrochlorination of ethylene.[11]

TABLE 49. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR ETHYL CHLORIDE PRODUCTION BY THE HYDROCHLORINATION OF ETHYLENE[11]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	34,019
E. I. du Pont de Nemours Co., Inc.	Deepwater, NJ	49,895
Ethyl Corp.	Baton Rouge, LA	95,254
Ethyl Corp.	Houston, TX	68,039
PPG Industries	Lake Charles, LA	54,431
Shell Chemical Co.	Houston, TX	38,555
Stauffer Chemical Co.	Long Beach, CA	45,359
Total capacity		385,552
Average capacity		55,079
Percent of total ethyl chloride capacity		83

2. Industry Production Trends

Historically, growth averaged 0.5% per year between 1965 and 1975 and is expected to decline between 30% and 50% per year through 1980.[11]

Table 50 gives the major uses for ethyl chloride.[11]

Tetraethyl lead, which is cheaper than tetramethyl lead, is by far the primary antiknock compound used in gasoline. EPA regulations require refiners to reduce the average lead content of gasoline to 0.5 gram per gallon, a reduction of from 75% to 80% from current levels, within 2 years.[11] The number of new cars burning unleaded fuel exclusively may cause the disappearance of antiknock lead compounds from the market.[11]

3. Outlook

Producers and petroleum refiners expect lead alkyl antiknock compounds to totally disappear from the market by the mid-1980's. Ethyl chloride plants can be converted to manufacture other, fast-growing hydrocarbons such as methylene chloride.[11]

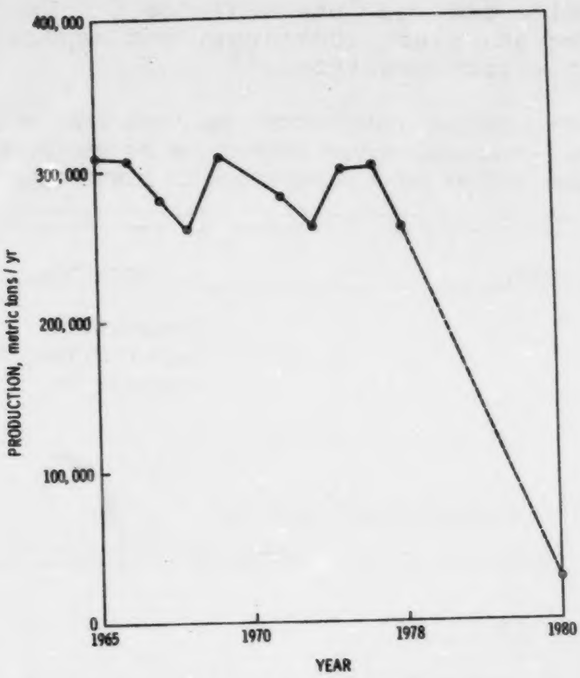

Figure 43. Ethyl chloride production, 1965 to 1980[11,64-72]

TABLE 50. ETHYL CHLORIDE CONSUMPTION IN 1975[11]

Use	Percent
Tetraethyl lead antiknock compounds	90
Export and miscellaneous	10
TOTAL	100

K. 1,1,1-TRICHLOROETHANE

1. Present Technology

In 1975 total U.S. capacity for 1,1,1-trichloroethane was estimated to be 3.36 x 10^5 metric tons/yr. 1,1,1-Trichloroethane represents 2.9% of all major chlorinated hydrocarbon capacity. The production in 1975 was 2.79 x 10^5 metric tons. Major producers in the United States are Dow Chemical Co., PPG Industries, Inc., and Vulcan Materials Co. The three companies produce 1,1,1-trichloroethane at three locations. About 7% of the total domestic capacity for 1,1,1-trichloroethane manufacture is based on ethylene dichloride-derived intermediates.[28] Table 51 lists manufacturing companies, plant locations, and capacities for the manufacture of 1,1,1-trichloroethane.[28]

TABLE 51. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR 1,1,1-TRICHLOROETHANE PRODUCTION BY THE HYDROCHLORINATION AND CHLORINATION OF VINYL CHLORIDE[28]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	204,116
PPG Industries	Lake Charles, LA	79,378
Vulcan Materials Co.	Geismar, LA	29,483
Total capacity		312,977
Average capacity		104,326
Percent of total 1,1,1-trichloroethane capacity		93

2. Industry Production Trends

Historically, growth averaged over 11.7% per year from 1966 through 1974 and is expected to be 4% per year through 1979. Figure 44 shows production for 1,1,1-trichloroethane between 1966 and 1979.[64-72]

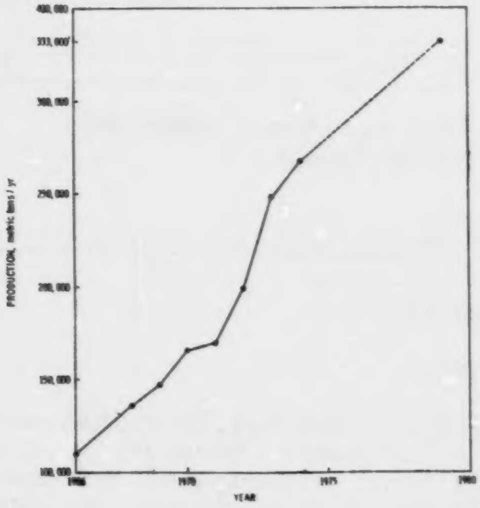

Figure 44. 1,1,1-Trichloroethane production, 1966 to 1979.[64-72]

Table 52 summarizes the data for 1,1,1-trichloroethane uses.

TABLE 52. 1,1,1-TRICHLOROETHANE CONSUMPTION IN 1975[28]

Use	Percent
Cleaning solvent cold cleaning	33.0
Cleaning solvent vapor degreasing	29.6
Vinylidene chloride	20.5
Exports	11.8
Miscellaneous	5.1
TOTAL	100.0

1,1,1-Trichloroethane is well suited for use as a solvent in hot and cold cleaning of metals and other materials because of its nonflammability, excellent solvent properties, and low toxicity. With a restriction on the use of trichloroethylene, many vapor degreasing operations have switched to 1,1,1-trichloroethane. Consumption of 1,1,1-trichloroethane for vapor degreasing increased at an average annual rate of 21% from 1971 through 1974.

1,1,1-Trichloroethane is used as a vapor pressure depressant in aerosols, as a coolant in metal cutting oils, as a solvent, as a carrier for lubricants, and in the manufacture of vinylidene chloride which is consumed chiefly in the production of polyvinylidene copolymers.

3. Outlook

To meet the projected growth rate of 4% per year, additional capacity will be required by 1977-78. This is expected since Dow is expanding its 1,1,1-trichloroethane facilities at Freeport, Texas and Plaquemine, Louisiana.

1,1,1-Trichloroethane's growth in cleaning operations is expected to continue, but at a lower rate, unless trichloroethylene is confirmed to be carcinogenic.

Consumption of 1,1,1-trichloroethane for vinylidene chloride production and air aerosols is expected to remain static.

L. TRICHLOROETHYLENE

1. Present Technology

In 1975 total U.S. capacity for trichloroethylene was estimated to be 2.18×10^5 metric tons/yr.[10] This represents 1.9% of all chlorinated hydrocarbon capacity. The production in 1975 was 1.61×10^5 metric tons.[10] The major producers in the

United States are Diamond Shamrock Corp., Dow Chemical U.S.A., Ethyl Corp., Occidental Petroleum Corp., and PPG Industries, Inc. These five companies manufacture trichloroethylene at five locations.[10]

Trichloroethylene is produced commercially by two processes: (1) oxyhydrochlorination of ethylene dichloride and (2) chlorination then dehydrochlorination of acetylene. Oxyhydrochlorination of ethylene dichloride is the major process and accounts for 92% of the industrial capacity.

Chlorination then dehydrochlorination of acetylene currently accounts for 8% of industrial capacity. It was the original method of production, although Occidental Petroleum Corp. is the only company producing trichloroethylene by this process. Its main drawbacks are its relatively expensive starting raw material and the expense involved in recovering the chlorine value from the byproduct hydrochloric acid produced. Table 53 lists manufacturing companies, plant locations, and capacities for the manufacture of trichloroethylene by the oxyhydrochlorination of ethylene dichloride.[10]

TABLE 53. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR TRICHLOROETHYLENE PRODUCTION BY THE OXYHYDROCHLORINATION OF ETHYLENE DICHLORIDE.[10]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	68,039
Diamond Shamrock	Deer Park, TX	22,680
Ethyl Corp.	Baton Rouge, LA	18,144
PPG Industries	Lake Charles, LA	90,718
Total capacity		199,580
Average capacity		49,895
Percent of total trichloroethylene capacity		92

2. Industry Production Trends

Historically, growth averaged 1.25% per year between 1964 and 1974 and is expected to decline 8% per year through 1979.[10] Figure 45 shows production capacity from 1945 through 1979.[10,64-72]

Table 54 gives the major uses for trichloroethylene.[10]

Trichloroethylene has been widely acclaimed to be the best solvent for use in vapor degreasing, but it is very photoreactive. Current air pollution regulations severely restrict use and emissions of trichloroethylene in vapor-degreasing plants. Emission reduction requires removal of trichloroethylene vapors and recycling. This also reduces overall demand at degreasing plants.[10] Evidence

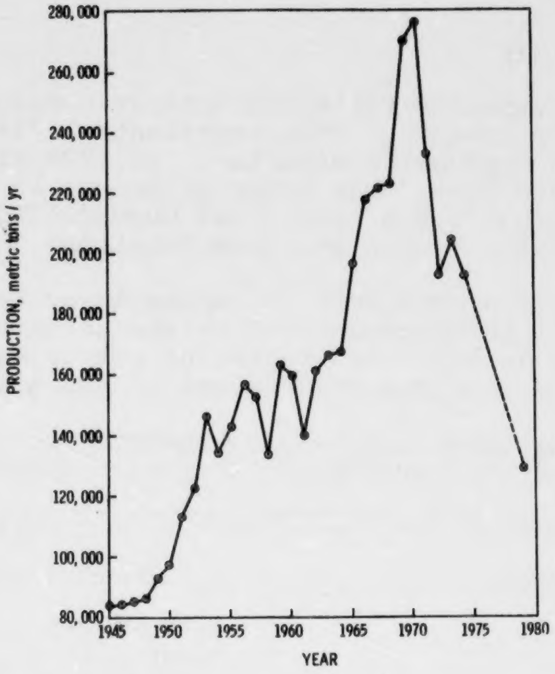

Figure 45. Trichloroethylene production, 1945 to 1979.[10,64-72]

TABLE 54. TRICHLOROETHYLENE CONSUMPTION IN 1975[10]

Use	Percent
Vapor degreasing of fabricated metal parts	87
Exports	11
Miscellaneous	2
TOTAL	100

that trichloroethylene is a potential carcinogen has also affected its market, causing significant decreases in production.[10]

3. Outlook

A steady decline in the use of trichloroethylene as a degreasing solvent is currently taking place.[10] Alternative solvents such as perchloroethylene and 1,1,1-trichloroethane are being substituted for trichloroethylene. It is likely in the future that trichloroethylene will be totally phased out in favor of alternative chlorinated solvents.[10]

M. EPICHLOROHYDRIN

1. Present Technology

In 1975 total U.S. capacity for epichlorohydrin was estimated to be 2.04×10^5 metric tons/yr. This represents 1.78% of all chlorinated hydrocarbon production capacity. In 1975 the production was 1.71×10^5 metric tons. The major producers in the United States are Dow Chemical U.S.A. and Shell Chemical Co. The two companies produce epichlorohydrin at three locations.

Commercially, all epichlorohydrin is manufactured by the chlorohydrination of allyl chloride derived by the chlorination of propylene.[28] Table 55 lists manufacturing companies, plant locations, and capacities for the manufacture of epichlorohydrin.[28]

TABLE 55. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR EPICHLOROHYDRIN PRODUCTION BY THE CHLOROHYDRINATION OF ALLYL CHLORIDE[28]

Company	Location	Capacity, metric tons/yr
Dow Chemical U.S.A.	Freeport, TX	113,398
Shell Oil Company	Houston, TX	63,503
Shell Oil Company	Norco, LA	27,215
Total capacity		204,116
Average capacity		68,039
Percent of total epichlorohydrin capacity		100

2. Industry Production Trends

Historically, growth for refined epichlorohydrin averaged 8.5% per year between 1969 and 1973. Growth of crude epichlorohydrin has averaged a decline of 4% per year from 1967 through 1973.[28] Figure 46 shows actual and predicted production from 1962 through 1978 for refined epichlorohydrin and from 1967 through 1978 for crude epichlorohydrin.[28,64-72]

Table 56 gives the major uses for epichlorohydrin.[28]

Consumption of crude epichlorohydrin to make synthetic glycerin has declined since 1967 mainly because alternate raw materials, acrolein and propylene oxide, are now being used. The remaining crude product is being used to make refined epichlorohydrin to meet demands for increasing epoxy resins manufacture.28

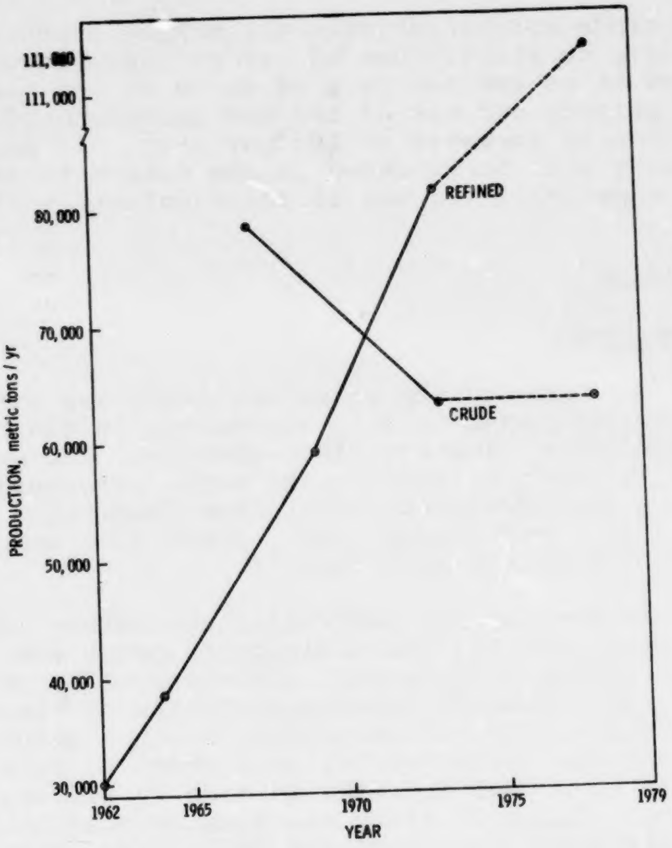

Figure 46. Epichlorohydrin production, 1962 to 1978.[28,64-72]

TABLE 56. EPICHLOROHYDRIN CONSUMPTION IN 1975[28]

Use	Percent	
	Crude epichlorohydrin	Refined epichlorohydrin
Synthetic glycerin	46.4	0
Epoxy resins	38.8	72.2
Epichlorohydrin elastomers	1.7	3.3
Other products	9.3	17.3
Exports	3.8	7.2
TOTAL	100.0	100.0

3. Outlook

Consumption of crude epichlorohydrin for making synthetic glycerin will remain fairly constant. Use of refined epichlorohydrin is expected to grow at an average rate of 6% to 7% per year. Epoxy resins are the primary end use of refined epichlorohydrin, and these are expected to increase at 10% per year. It is possible that U.S. capacity will be expanded in the future to meet the growing U.S. need, expecially for use in the manufacture of epoxy resins.[28]

N. PROPYLENE OXIDE

1. Present Technology

In 1975 total U.S. capacity for propylene oxide was estimated to be 11.93×10^5 metric tons.[12] This represents 10.42% of all major chlorinated hydrocarbon manufacturing capacity. The production in 1975 was 6.80×10^5 metric tons.[12] The major producers in the United States are BASF Wyandotte Corp., Dow Chemical U.S.A., Olin Corp., Oxirane Corp., and Texaco, Inc. These five companies produce propylene oxide at six locations.[12]

Propylene oxide is made by two industrial processes: chlorohydrination of propylene and peroxidation of propylene. Although it is not a chlorinated hydrocarbon, propylene oxide is being considered in this study because approximately 65% of the material is produced by the chlorohydrination process using a chlorinated hydrocarbon (propylene chlorohydrin) as a chemical intermediate. The remaining 35% of propylene oxide is made by Oxirane's peroxidation of propylene. Table 57 lists the four manufacturing companies, with their plant locations and capacities, that manufacture propylene oxide by chlorohydrination of propylene.[12]

TABLE 57. MANUFACTURERS, PLANT LOCATIONS, AND CAPACITIES FOR PROPYLENE OXIDE PRODUCTION BY THE CHLOROHYDRINATION OF PROPYLENE[12]

Company	Location	Capacity, metric tons/yr
BASF Wyandotte Corp.	Wyandotte, MI	79,378
Dow Chemical U.S.A.	Freeport, TX	415,035
Dow Chemical U.S.A.	Plaquemine, LA	154,221
Jefferson Chemical Co.	Port Neches, TX	68,039
Olin Corp.	Brandenburg, KY	58,967
Total capacity		775,640
Average capacity		155,128
Percent of total propylene oxide capacity		65

2. Industry Production Trends

Historically, growth averaged 12% per year between 1965 and 1975 and is expected to be 13% in 1976 and 10% per year between 1977 and 1980.[12] Figure 47 shows actual and predicted production of propylene oxide between 1965 and 1980.[12,64-72]

Table 58 gives the major uses for propylene oxide.[12]

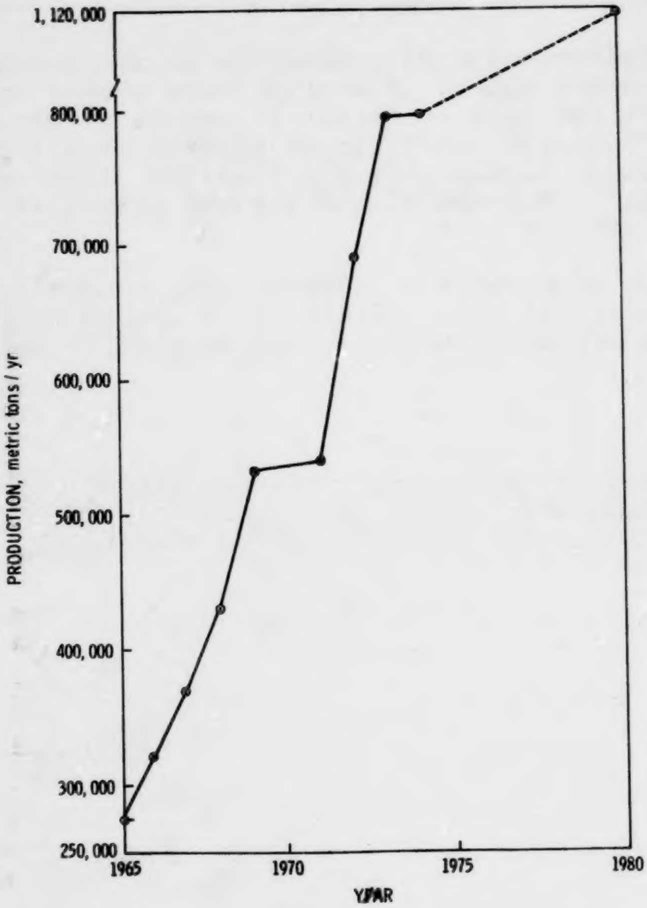

Figure 47. Propylene oxide production, 1965 to 1980.[12,64-72]

TABLE 58. PROPYLENE OXIDE CONSUMPTION IN 1975[12]

Use	Percent
Polypropylene glycol and polyether polyols for urethanes	58
Propylene glycol	24
Dipropylene glycol	5
Surfactants	6
Glycol ethers and miscellaneous	7
TOTAL	100

Demand for propylene oxide will continue as the urethane sector increases its market share. Flexible foams should continue to grow at 8% to 9% per year or better if exterior auto parts develop as predicted.[12] Energy conservation efforts should promote both rigid (construction insulation) and flexible (light-weight autos) urethane growth.[12] Growths of unsaturated polyester is expected to continue at 10% per year.

Long-term growth of propylene oxide depends on construction trends and the flammability issue. Little or no growth is expected in the nonurethane polyester sectors, and no significant new uses are forecast.[12]

3. Outlook

Until 1980, based on expansions currently taking place, no supply difficulty is expected. A new plant, with capacity ranging between 1.81×10^5 and 2.27×10^5 metric tons, will be required in the early 1980's.[12]

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73. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

74. Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

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77. Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

78. Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^{\epsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

APPENDIX A

DERIVATION OF SOURCE SEVERITY EQUATIONS[a]

1. SUMMARY OF MAXIMUM SEVERITY EQUATIONS

The maximum severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, and the ambient air quality standard, AAQS. The equations summarized in Table A-1 are developed in detail in this appendix.

TABLE A-1. POLLUTANT SEVERITY EQUATIONS FOR ELEVATED SOURCES

Pollutant	Severity equation
Particulate	$S = \frac{70\ Q}{H^2}$
SO_x	$S = \frac{50\ Q}{H^2}$
NO_x	$S = \frac{315\ Q}{H^{2.1}}$
Hydrocarbons	$S = \frac{162\ Q}{H^2}$
CO	$S = \frac{0.78\ Q}{H^2}$

2. DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is:[73]

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[a] This appendix was prepared by T. R. Blackwood and E. C. Eimutis, Monsanto Research Corporation, Dayton Laboratory, Dayton, Ohio.

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[73] Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

$$\chi = \frac{Q}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{Y}{\sigma_y}\right)^2\right]\exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-1)}$$

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3

Q = mass emission rate, g/s

σ_y = standard deviation of horizontal dispersion, m

σ_z = standard deviation of vertical dispersion, m

u = wind speed, m/s

y = horizontal distance from centerline of dispersion, m

H = height of emission release, m

x = downwind emission dispersion distance from source of emission release, m

π = 3.1416

We assume that χ_{max} occurs when $x>>0$ and $y = 0$. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows:[74]

$$\sigma_y = ax^b \qquad \text{(A-2)}$$

$$\sigma_z = cx^d + f \qquad \text{(A-3)}$$

Values for a, b, c, d, and f are given in Tables A-2 and A-3. Substituting these general equations into Equation A-1 yields:

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi ufx^b}\exp\left[-\frac{H^2}{2(cx^d + f)^2}\right] \qquad \text{(A-4)}$$

Assuming that χ_{max} occurs at $x<100$ m and the stability class is C, then $f = 0$ and Equation A-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}}\exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \qquad \text{(A-5)}$$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

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[74] Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

TABLE A-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a,33]

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a] For Equation A-2: $\sigma_y = ax^b$

where x = downwind distance
$b = 0.9031$

TABLE A-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a,74]

Usable range	Stability class	Coefficient		
		c_1	d_1	f_1
>1,000 m	A	0.00024	2.094	-9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2
100 to 1,000 m	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	f_3
<100 m	A	0.192	0.936	0
	B	0.156	0.922	0
	C	0.116	0.905	0
	D	0.079	0.881	0
	E	0.063	0.871	0
	F	0.053	0.814	0

[a] For Equation A-3: $\sigma_z = cx^d + f$

so that Equation A-5 reduces to:

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^2 d}\right] \qquad \text{(A-6)}$$

Taking the first derivative of Equation A-6

$$\frac{d\chi}{dx} = A_R \left\{ x^{-b-d}\left[\exp\left(B_R x^{-2d}\right)\right]\left(-2dB_R x^{-2d-1}\right) \right.$$

$$\left. + \exp\left(B_R x^{-2d}\right)\left(-b-d\right)x^{-b-d-1}\right\} \qquad \text{(A-7)}$$

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1}\left(\exp\left[B_R x^{-2d}\right]\right)\left(-2dB_R x^{-2d} -b-d\right) \qquad \text{(A-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-2dB_R x^{-2d} -d-b = 0 \qquad \text{(A-9)}$$

Therefore

$$(b+d)x^{2d} = -2dB_R \qquad \text{(A-10)}$$

or

$$x^{2d} = \frac{-2dB_R}{b+d} = \frac{2d\ H^2}{2c^2(b+d)} = \frac{d\ H^2}{c^2(b+d)} \qquad \text{(A-11)}$$

Hence

$$x = \left(\frac{d\ H^2}{c^2(b+d)}\right)^{1/2d} \text{ at } \chi_{max} \qquad \text{(A-12)}$$

Thus Equations A-2 and A-3 (at f = 0) become:

$$\sigma_y = a\left(\frac{d\ H^2}{c^2(d+b)}\right)^{b/2d} \qquad \text{(A-13)}$$

$$\sigma_z = c\left(\frac{d\ H^2}{c^2(b+d)}\right)^{d/2d} = \left(\frac{d\ H^2}{b+d}\right)^{1/2} \qquad \text{(A-14)}$$

The maximum will be determined for U.S. average conditions of stability. According to Gifford,[76] this is when $\sigma_y = \sigma_z$. Since $b = 0.9031$, and upon inspection of Table A-2 under U.S. average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \leq d \leq 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d in Equations A-13 and A-14 or:

$$\sigma_z = \frac{H}{\sqrt{2}} \qquad \text{(A-15)}$$

and

$$\sigma_y = \frac{a}{c}\ \frac{H}{\sqrt{2}} \qquad \text{(A-16)}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and $a = c$ if $b = d$ and $f = 0$ (between class C and D, but closer to belonging in class C).

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \qquad \text{(A-17)}$$

Substituting for σ_y from Equation A-17 and for σ_z from Equation A-15 into Equation A-1 and letting $y = 0$:

$$\chi_{max} = \frac{2\ Q}{\pi u H^2}\ \exp\left[-\ \frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \qquad \text{(A-18)}$$

or

$$\chi_{max} = \frac{2\ Q}{\pi e u H^2} \qquad \text{(A-19)}$$

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[a] The values given in Table A-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two.

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[76] Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

3. DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

Source severity, S, has been defined as follows:

$$S = \frac{\bar{\chi}_{max}}{AAQS} \qquad \text{(A-20)}$$

where $\bar{\chi}_{max}$ = time-averaged maximum ground level concentration
AAQS = ambient air quality standard

Values of $\bar{\chi}_{max}$ are found from the following equation:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_0}{t}\right)^{0.17} \qquad \text{(A-21)}$$

where t_0 is the "instantaneous" (i.e., 3-minute) averaging time and t is the averaging time used for the ambient air quality standard as shown in Table A-4.

a. CO Severity

The primary standard for CO is reported for a 1-hr averaging time. Therefore, t = 60 minutes. Hence, from Equation A-21:

$$\bar{\chi}_{max} = \bar{\chi}_{max} \left(\frac{3}{60}\right)^{0.17} \qquad \text{(H-22)}$$

Substituting for χ_{max} from Equation A-19 yields:

$$= \frac{2\ Q}{\pi e u H^2} \left(\frac{3}{60}\right)^{0.17} \qquad \text{(A-23)}$$

$$= \frac{2\ Q}{(3.14)(2.72)(4.5)H^2} (0.6) \qquad \text{(A-24)}$$

$$= \frac{0.052\ Q}{H^2} (0.6)$$

or

$$\bar{\chi}_{max} = \frac{3.12 \times 10^{-2}\ Q}{H^2} \qquad \text{(A-25)}$$

Substituting the primary standard for CO (0.04 g/m^3) and the value for $\bar{\chi}_{max}$ from Equation A-25 into the equation for S (Equation A-20) then gives:

TABLE A-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS[77]

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate	Annual (geometric mean)	75 $\mu g/m^3$	60[a] $\mu g/m^3$
	24 hr[b]	260 $\mu g/m^3$	150 $\mu g/m^3$
Sulfur oxides	Annual (arithmetic mean)	80 $\mu g/m^3$ (0.03 ppm)	60 $\mu g/m^3$ (0.02 ppm)
	24 hr[b]	365 $\mu g/m^3$ (0.14 ppm)	260[c] $\mu g/m^3$ (0.1 ppm)
	3 hr[b]	none	1,300 $\mu g/m^3$ (0.5 ppm)
Carbon monoxide	8 hr[b]	10,000 $\mu g/m^3$ (9 ppm)	none
	1 hr[b]	40,000 $\mu g/m^3$ (35 ppm)	(Same as primary)
Nitrogen dioxide	Annual (arithmetic mean)	100 $\mu g/m^3$ (0.05 ppm)	(Same as primary)
Photochemical oxidants	1 hr[b]	160 $\mu g/m^3$ (0.08 ppm)	(Same as primary)
Hydrocarbons (nonmethane)	3 hr (6 to 9 a.m.)	160 $\mu g/m^3$ (0.24 ppm)	(Same as primary

[a] The secondary annual standard (60 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the 24-hr secondary standard.

[b] Not to be exceeded more than once per year.

[c] The secondary annual standard (260 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the annual standard.

$$S = \frac{\overline{X}_{max}}{AAQS} = \frac{3.12 \times 10^{-2}\ Q}{0.04\ H^2} \tag{A-26}$$

or

$$S_{CO} = \frac{0.78\ Q}{H^2} \tag{A-27}$$

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[77] Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

b. Hydrocarbon Severity

The primary standard for hydrocarbon is reported for a 3-hr averaging time. Therefore, t = 180 minutes. Hence, from Equation A-21:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} = 0.5\chi_{max} \qquad \text{(A-28)}$$

Substituting for χ_{max} from Equation A-19 yields:

$$\bar{\chi}_{max} = \frac{(0.5)(0.052)\ Q}{H^2} = \frac{0.026\ Q}{H^2} \qquad \text{(A-29)}$$

For hydrocarbons, AAQS = 1.6×10^{-4} g/m³. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \qquad \text{(A-30)}$$

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \qquad \text{(A-31)}$$

c. Particulate Severity

The primary standard for particulate is reported for a 24-hr averaging time. Therefore, t - 1,440 minutes. Hence, for Equation A-21:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{1,440}\right)^{0.17} \qquad \text{(A-32)}$$

Substituting for χ_{max} from Equation A-19 yields:

$$\bar{\chi}_{max} = \frac{0.052\ Q}{H^2}\ (0.35) = \frac{0.0182\ Q}{H^2} \qquad \text{(A-33)}$$

For particulates, AAQS = 2.6×10^{-4} g/m³. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \qquad \text{(A-34)}$$

or

$$S_P = \frac{70\ Q}{H^2} \qquad \text{(A-35)}$$

d. SO_x Severity

The primary standard for SO_x is reported for a 24-hr averaging time. Therefore, t = 1,440 minutes. Hence, proceeding as before:

$$\bar{\chi}_{max} = \frac{0.0182\ Q}{H^2} \qquad (A-36)$$

For SO_x, AAQS = 3.65×10^{-4} g/m³. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.0182\ Q}{3.65 \times 10^{-4}\ H^2} \qquad (A-37)$$

or

$$S_{SO_x} = \frac{50\ Q}{H^2} \qquad (A-38)$$

e. NO_x Severity

Since NO_x has a primary standard with a 1-yr averaging time, the χ_{max} correction equation (Equation A-21) cannot be used. Alternatively, the following equation is used:

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (A-39)$$

A difficulty arises, however, because a distance, x, from emission point to receptor, is included in Equation A-39. Hence, the following rationale is used: Equation A-19 is valid for neutral conditions or when $\sigma_z = \sigma_y$. This maximum occurs when

$$H \simeq \sqrt{2}\sigma_z$$

and since, under these conditions,

$$\sigma_z = ax^b$$

then the distance x_{max} where the maximum concentration occurs is:

$$x_{max} = \left(\frac{H}{\sqrt{2}a}\right)^{1/b} \qquad (A-40)$$

For Class C conditions, a = 0.113 and b = 0.911. Substituting these values into Equation A-40 yields:

$$x_{max} = \frac{H^{1.098}}{0.16} = 7.5\ H^{1.098} \qquad (A-41)$$

Since

$$\sigma_z = 0.113\ x_{max}^{0.911}$$

and

$$u = 4.5\ \text{m/s}$$

and letting $x = x_{max}$, Equation A-39 becomes:

$$\bar{\chi}_{max} = \frac{4\ Q}{x_{max}^{1.911}}\ \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-42)}$$

In Equation A-42, the factor

$$\frac{4\ Q}{x_{max}^{1.911}} = \frac{4\ Q}{(7.5\ H^{1.098})^{1.911}} \qquad \text{(A-43)}$$

Therefore,

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}}\ \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-43)}$$

As noted above,

$$\sigma_z = 0.113\ x^{0.911}$$

Substitution for x from Equation A-41 into the above equation yields:

$$\sigma_z = 0.113\ (7.5\ H^{1.1})^{0.911} = 0.71\ H \qquad \text{(A-44)}$$

Substituting for σ_z from Equation A-44 into Equation A-42 yields:

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}}\ \exp\left[-\frac{1}{2}\left(\frac{H}{0.71\ H}\right)^2\right] \qquad \text{(A-45)}$$

$$= \frac{0.085\ Q}{H^{2.1}}\ (0.371) = \frac{3.15 \times 10^{-2}\ Q}{H^{2.1}} \qquad \text{(A-46)}$$

Since the NO_x standard is 1.0×10^{-4} g/m^3, the NO_x severity equation is:

$$S_{NO_x} = \frac{\bar{\chi}_{max}}{AAQS} = \frac{3.15 \times 10^{-2}\ Q}{1 \times 10^{-2}\ H^{2.1}} \qquad \text{(A-47)}$$

or

$$S_{NO_x} = \frac{315\ Q}{H^{2.1}} \qquad \text{(A-48)}$$

4. AFFECTED POPULATION CALCULATION

Another form of the plume dispersion equation is needed to calculate the affected population since the population is assumed to be distributed uniformly around the source. If the wind directions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration, $\bar{\chi}$, in g/m^3 is then:[74]

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-49)}$$

To find the distances at which $\bar{\chi}$/AAQS = 1.0, roots are determined for the following equation:

$$\frac{2.03\ Q}{(\mathrm{AAQS})\ \sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] = 1.0 \qquad \text{(A-50)}$$

keeping in mind that:

$$\sigma_z = ax^b + c$$

where a, b, and c are functions of atmospheric stability and are assumed to be selected for stability Class C. Since Equation A-50 is a transcendental equation, the roots are found by an iterative technique using the computer.

For a specified emission from a typical source, $\bar{\chi}$/AAQS as a function of distance might look as follows:

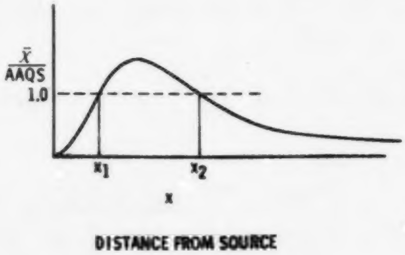

Figure A-1. $\frac{\chi}{AAQS}$ as a function of distance.

The affected population is contained in the area

$$A = \pi(x_2{}^2 - x_1{}^2) \qquad \text{(A-51)}$$

If the affected population density is D_P, the total affected population, P, is

$$P = D_P A \text{ (persons)} \qquad \text{(A-52)}$$

APPENDIX B

FIELD SAMPLING RESULTS

1. DIRECT CHLORINATION - CARBON TETRACHLORIDE PRODUCTION

Field sampling was performed at a plant producing carbon tetrachloride by the direct chlorination process.

The sites sampled included the following:

- Inlet to scrubber
- Outlet from scrubber
- Waste system sniffer
- Chlorocarbon sniffer

At each of the four sites, tests were performed to measure concentrations of hydrocarbons, chlorine and chlorides in the stack. Tests performed included the following:

- Determination of chlorine/chloride
- Determination of the concentration of low molecular weight hydrocarbons using Tedlar® gas bags.
- Determination of the concentration of high molecular weight hydrocarbons using HVOSS sampling train.

Results of the tests performed are presented in Tables B-1 through B-4. The stack gas concentrations are summarized in units of grams per cubic meter and emission factors in grams per kilogram of carbon tetrachloride produced.

2. CHLOROHYDRINATION - PROPYLENE OXIDE PRODUCTION

Field sampling was performed at a plant producing propylene oxide by the chlorohydrination of propylene. The sites sampled by MRC include the following:

- Feed line to flare and/or boilerhouse
- Combusted gases from boilerhouse

TABLE B-1. ATMOSPHERIC EMISSIONS FROM SCRUBBER INLET

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride:	
Chlorine/chloride	66.2 ± 79%
GC/FID bag samples:	
CH_4 equivalents	2.5
GC/MS HVOSS:	
Dichloromethoxy phenol	8.7×10^{-5}
Trichloromethoxy phenol	4.5×10^{-4}
GC - C_7 - C_{16} Hydrocarbons:	
C_7	4.1×10^{-3}
C_8	1.7×10^{-2}
C_{10}	1.9×10^{-2}
C_{11}	1.7×10^{-2}
C_{12}	6.1×10^{-1}
C_{13}	9.3×10^{-2}
C_{14}	9.0×10^{-3}
C_{15}	2.4×10^{-2}
C_{16}	1.3×10^{-3}
$>C_{16}$	4.0×10^{-2}

TABLE B-2. ATMOSPHERIC EMISSIONS FROM SCRUBBER OUTLET
(Stack height: 25 meters)

Material emitted by tests performed	Concentration of emission, g/m^3	Emission factor, g/kg
Chlorine/chloride:		
Chlorine/chloride	ND	-
GC/FID bag samples:		
CH_4 equivalent	0.14	1.1×10^{-2}
GC/MS HVOSS:	-	-
GC - C_7 - C_{16} hydrocarbon:		
C_{11}	8.7×10^{-4}	6.6×10^{-5}
C_{12}	1.3×10^{-3}	9.8×10^{-5}
C_{13}	2.6×10^{-4}	2.0×10^{-5}
C_{14}	1.1×10^{-2}	8.3×10^{-4}
C_{15}	1.1×10^{-3}	8.3×10^{-5}
C_{16}	4.7×10^{-5}	3.6×10^{-6}
$>C_{16}$	6.5×10^{-4}	4.9×10^{-5}

TABLE B-3. ATMOSPHERIC EMISSIONS FROM WASTE SYSTEM
(Stack height: 7.6 meters)

Material emitted by tests performed	Concentration of emission, g/m^3	Emission factor, g/kg
Chlorine/chloride:		
Chlorine/chloride	ND	-
GC/FID bag samples:		
CH_4 equivalent	4.3×10^{-2}	2.0×10^{-2}
GC/MS HVOSS:	-	-
GC - C_7 - C_{16} hydrocarbon:		
C_7	6.0×10^{-5}	2.8×10^{-5}
C_{12}	2.6×10^{-2}	1.2×10^{-2}
C_{13}	2.9×10^{-2}	1.3×10^{-2}
C_{14}	7.1×10^{-3}	3.3×10^{-3}
C_{15}	5.3×10^{-3}	2.5×10^{-3}
C_{16}	3.3×10^{-4}	1.5×10^{-4}
$>C_{16}$	2.5×10^{-2}	1.2×10^{-2}

TABLE B-4. ATMOSPHERIC EMISSIONS FROM CHLOROCARBON SYSTEM
(Stack height: 6.1 meters)

Material emitted by tests performed	Concentration of emission, g/m^3	Emission factor, g/kg
Chlorine/chloride:		
Chlorine/chloride	ND	-
GC/FID bag samples:		
CH_4 equivalent	3.2×10^{-2}	1.2×10^{-2}
CCl_4 equivalent	18.0	6.7
GC/MS HVOSS:		
Trichlorobenzene	8.2×10^{-6}	3.1×10^{-6}
Trichloromethoxy phenol	8.8×10^{-5}	3.3×10^{-5}
GC C_7 - C_{16} hydrocarbon:		
C_7	1.2×10^{-3}	4.5×10^{-4}
C_9	9.3×10^{-4}	3.5×10^{-4}
C_{10}	4.4×10^{-4}	1.6×10^{-4}
C_{11}	5.5×10^{-5}	2.0×10^{-5}
C_{12}	5.5×10^{-5}	2.0×10^{-5}
C_{13}	5.5×10^{-5}	2.0×10^{-5}
C_{15}	1.6×10^{-4}	6.0×10^{-5}
C_{16}	2.2×10^{-4}	8.2×10^{-5}
$>C_{16}$	3.3×10^{-4}	1.2×10^{-4}

At each of the two sites tests were performed to measure concentrations of hydrocarbons and chlorine/chlorides present in the lines. Tests performed included the following:

- Determination of chlorine/chloride concentration
- Determination of low molecular weight hydrocarbon concentration using Tedlar® gas bags for sample collection
- Determination of high molecular weight hydrocarbon concentration using HVOSS sampling train

Results of the tests performed are presented in Tables B-5 and B-6. The stack gas concentrations are summerized in units of grams per cubic meter and emissions factors in grams per kilogram of propylene oxide produced.

3. DIRECT CHLORINATION - MONOCHLOROBENZENE PRODUCTION

Field sampling was performed at a plant producing monochlorobenzene by the direct chlorination of benzene. The sites sampled included the following:

- Process vent
- Benzene storage tank
- Intermediate storage tank
- Monochlorobenzene storage tank

At each of the four sites tests were performed to measure concentration of material present. The tests performed included the following:

- Determination of chlorine/chloride concentration
- Determination of low molecular weight hydrocarbons using Tedlar® gas bags for sample collection

In addition, concentration of high molecular weight hydrocarbons at the process vent were measured using the HVOSS sampling train.

The results of the tests performed are presented in Tables B-7, B-8, B-9, and B-10. The gas concentrations are summarized in units of grams per cubic meter and emission factors in grams per kilogram of monochlorobenzene produced.

4. OXYHYDROCHLORINATION - ETHYLENE DICHLORIDE PRODUCTION

Field sampling was performed at a plant producing ethylene dichloride by the oxyhydrochlorination of ethylene. The sites sampled included the following:

TABLE B-5. ATMOSPHERIC EMISSIONS FROM BOILERHOUSE OUTLET
(Stack height: 60 meters)

Material emitted by tests performed	Concentration of emission, g/m^3	Emission factor, g/kg
Chlorine/chloride:		
Chlorine/chloride	9.4×10^{-3} ± 60%	8.8×10^{-2}
GC/FID bag samples:		
Methane	4×10^{-3}	3.7×10^{-2}
GC/MS HVOSS:		
Dichloropropane	1.2	11.2
Trichloropropane	9×10^{-2}	8.4×10^{-1}
Dichloropropanol	9×10^{-2}	8.4×10^{-1}
Epichlorohydrin	2×10^{-2}	1.9×10^{-1}
Toluene	4×10^{-3}	3.7×10^{-2}
Ethyl benzene	2×10^{-3}	1.9×10^{-2}
Benzaldehyde	9×10^{-4}	8.4×10^{-3}
Bis(βchloro- iso propylether)	5×10^{-1}	4.7
Naphlalene	1×10^{-2}	9.4×10^{-2}
C_4-alkyl biphenyl	1×10^{-2}	9.4×10^{-2}
C_7-C_{16} hydrocarbons HVOSS:		
$<C_7$	3.4×10^{-4}	3.2×10^{-3}
C_7	1.4×10^{-4}	1.3×10^{-3}

TABLE B-6. ATMOSPHERIC EMISSIONS FROM BOILERHOUSE INLET
(Stack height: 60 meters)

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride:	
Chlorine/chloride	0.46 ± 129%
GC/FID bag samples:	
Methane	3.3
Ethene	13.3
GC/MS – bag samples:	
Propane	Detected
Propylene	Detected
Propylene oxide	Detected
Pentane	Detected
Propion aldelyde	Detected
Methyl propane	Detected
Butane	Detected
Chloropropene	Detected
1,2-Dichloropropane	Detected
GC/MS HVOSS:	
Dichloropropane	1.04
Epichlorohydrin	0.19
Trichloropropane	0.05
Bis(βchloro iso-propylether)	0.25
Naphthalene	0.01
C_4-Alkyl Biphenyl	0.002
C_{16}-C_{30} Aliphatics	0.01
C_7-C_{16} hydrocarbons HVOSS:	
C_7	12.1
C_8	1.8×10^{-2}
C_9	1.3×10^{-2}
C_{10}	3.2×10^{-2}
C_{11}	2.5×10^{-4}
C_{15}	1.6×10^{-3}
C_{16}	1.2×10^{-3}

TABLE B-7. ATMOSPHERIC EMISSIONS FROM PROCESS STACK
(Stack height: 10 meters)

Material emitted by tests performed	Concentration of emission, g/m^3	Emission factor, g/kg
Chlorine/chloride:		
Chlorine/chloride	2.2 ± 174%	5.6×10^{-2}
GC/FID bag samples:		
Benzene	8.2×10^{-2} ± 174%	2.1×10^{-3}
Monochlorobenzene	1.3 ± 221%	3.3×10^{-2}
GC/MS bag samples:		
Benzene	7.3×10^{-2}	1.9×10^{-3}
Monochlorobenzene	2.5×10^{-2}	6.4×10^{-4}
GC/MS HVOSS:		
Benzene	1.4×10^{-4}	3.5×10^{-6}
Toluene	5.9×10^{-6}	1.5×10^{-7}
Monochlorobenzene	4.5×10^{-3}	1.1×10^{-4}
Dichlorobenzene	1.3×10^{-4}	3.3×10^{-6}
Trichlorobenzene	5.4×10^{-6}	1.4×10^{-7}
Tetrachlorobenzene	4.1×10^{-6}	1.1×10^{-7}
Pentachlorobenzene	4.5×10^{-7}	1.1×10^{-8}
Bromobenzene	4.5×10^{-7}	1.1×10^{-8}
Ethyl styrene	5.2×10^{-5}	1.3×10^{-6}
Benzoic acid	6.6×10^{-4}	1.8×10^{-5}
Napthalene	8.3×10^{-5}	2.1×10^{-6}
C_7-C_{16} hydrocarbons HVOSS:		
C_7	1.4×10^{-3}	3.5×10^{-5}
C_8	2.4×10^{-2}	6.1×10^{-4}
C_9	3.4×10^{-4}	8.6×10^{-6}
C_{10}	9.8×10^{-4}	2.6×10^{-5}
C_{11}	1.6×10^{-4}	4.1×10^{-6}
C_{12}	7.0×10^{-4}	1.8×10^{-5}
C_{13}	5.5×10^{-4}	1.4×10^{-3}
C_{15}	9.4×10^{-4}	2.4×10^{-5}
$>C_{16}$	2.1×10^{-3}	5.4×10^{-5}

TABLE B-8. ATMOSPHERIC EMISSIONS FROM INTERMEDIATE STORAGE (Stack height: 10 meters)

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride:	
Chlorine/chloride	424 ± 82%
GC/FID bag sample:	
Benzene	44.4 ± 47%
Monochlorobenzene	3.0×10^{-1} ± 179%

TABLE B-9. ATMOSPHERIC EMISSIONS FROM MONOCHLOROBENZENE STORAGE

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride:	
Chlorine/chloride	3.1×10^{-1} ± 312%
GC/FID bag samples:	
Monochlorobenzene	6.2 ± 47%
Benzene	1.02 ± 171%

TABLE B-10. ATMOSPHERIC EMISSIONS FROM BENZENE STORAGE

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride:	
Chlorine/chloride	2.8 ± 42%
GC/FID bag sample:	
Benzene	71.2 ± 89%
Monochlorobenzene	6.2×10^{-1} ± 186%

- Oxy-vent
- Heads column
- High boils vent

At each of the three sites, tests were performed to measure concentrations of hydrocarbons, chlorine, chlorides, moisture, and flow rates of gases in the stacks. Tests performed included the following:

- Chlorine/chloride concentration determination
- Low molecular weight hydrocarbon concentration determination using Tedlar® gas samples
- High molecular weight hydrocarbon concentration determination using Porapak tubes
- Moisture contents of stack gases
- Flow rates of stack gases

Results of the tests performed are presented in Tables B-11 through B-13. The stack gas concentrations are summarized in units of grams per cubic meter.

TABLE B-11. ATMOSPHERIC EMISSIONS FROM OXY-VENT
(Stack height: 55 meters)

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride test:	
Chlorine/chloride	$5.5 \times 10^{-2} \pm 34\%$
Bag sample field analysis:	
Methane	28.6 ± 0%
Ethylene	9.6 ± 67%
Ethylene dichloride	13.3 ± 50%
Vinyl chloride	0.3 ± 246%
Porapak tube analysis:	
Methylene chloride	$<9.1 \times 10^{-2} \pm 140\%$
Chloroform	$<1.4 \times 10^{-1} \pm 242\%$
Carbon tetrachloride	$<9.1 \times 10^{-2} \pm 140\%$
Ethylene dichloride	27.7 ± 145%
Trichloroethane	$<1.4 \times 10^{-1} \pm 242\%$

TABLE B-12. ATMOSPHERIC EMISSIONS FROM HEADS COLUMN
(Stack height: 20 meters)

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride test:	
Chlorine/chloride	6.2×10^{-1} ± 180%
Bag sample field analysis:	
Vinyl chloride	27.9
Ethylene dichloride	92.8 ± 43%
Methylene chloride	3.5 ± 55%
Chloroform	97.1 ± 67%
Carbon tetrachloride	218.2 ± 84%
Ethyl chloride	108.0
Porapak tube analysis:	
Ethylene dichloride	17.2 ± 236%
1,1-Dichloroethane	9.2 ± 308%
Ethyl chloride	0.9 ± 142%
Vinylidene chloride	0.2 ± 229%
Dichloroethylene	1.8 ± 225%
Chloroform	73.5 ± 266%
Carbon tetrachloride	39.9 ± 258%
Methylene chloride	0.6 ± 293%

TABLE B-13. ATMOSPHERIC EMISSIONS FROM HIGH BOILS VENT
(Stack height: 12 meters)

Material emitted by tests performed	Concentration of emission, g/m^3
Chlorine/chloride test:	
Chlorine/chloride	47.9 ± 132%
Bag sample field analysis:	
Ethylene dichloride	442.0 ± 0%
Methane	0.04 ± 218%
Ethylene	0.11 ± 75%
Porapak tube analysis:	
Ethylene dichloride	321 ± 126%
Methylene chloride	0.13
Chloroform	0.13

APPENDIX C

FIELD SAMPLING METHODS

The field sampling methods presented here, and the analytical methods described in Appendix D were used to provide data on the major components of the gaseous compositions as well as information on the concentration and identification of organic compounds present at low levels. Data collected from the plants were in terms of concentration (ppm) in sample collected; this information was converted to concentration (g/m^3) in stack gas and emission factors (g/kg) using the amount of sample collected, flow rates, and production data.

1. HYDROCARBON

Engineering estimates of the composition of gas streams selected for field sampling indicated the presence of both low and high molecular weight hydrocarbons. Sampling techniques used are described in the following subsections.

a. Low Molecular Weight Hydrocarbons ($<C_6$)

The low molecular weight materials were collected in a gas sampling train and analyzed both on site and in the laboratory. The sampling equipment used for collecting the gas samples is shown in Figure C-1. The sampling train consisted of a glass probe, Teflon® sample line, Tedlar bag for collecting the sample, a rigid leakproof container, and an explosion-proof vacuum pump.

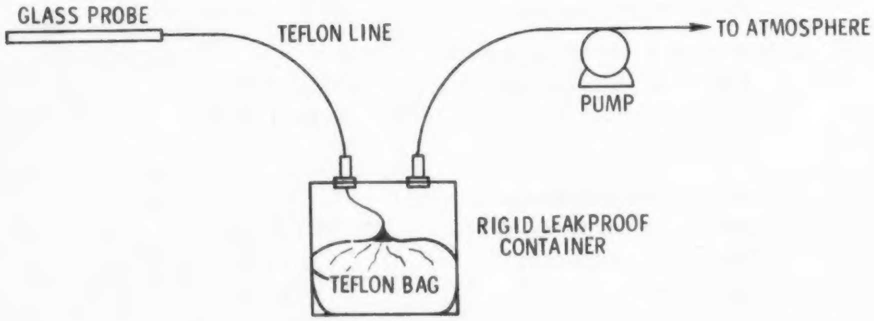

Figure C-1. Gas sampling train.

The gaseous samples collected in Tedlar bags were analyzed both on site for C_1 to C_6 hydrocarbons as well as in the laboratory for a wide range of organic compounds. On-site analytical procedures, although carried out by sampling personnel in the field, are described in the section under Analytical Procedures.

b. High Molecular Weight Hydrocarbons ($>C_6$) - SASS Module

High molecular weight hydrocarbons were collected using a porous polymer collection technique to trap and concentrate the materials for gas chromatography/mass spectrometry (GC/MS) analysis in the laboratory.

The sampling method included a high volume organic sampling system (HVOSS), which was a modification of the Source Assessment Sampling System (SASS) described in the EPA's Level I Environmental Assessment Procedures. The cydones and filter portions of the SASS train, normally employed to collect particulate from source streams, were removed and the remaining portion of the system was used to collect the organic materials. Thus, the sampling train was made up of a suitable probe maintained at stack temperature, the gas cooler module, the thermostated XAD-2 resin cartridge condensate condenser, cooling and silica gel impingers, and the control module. This system permitted the collection of a large quantity of organic components in a relatively short time. Figure C-2 shows a schematic diagram of the sampling train, and Figure C-3 shows the XAD-2 sorbent trap module.

The SASS train included four impingers. The first two impingers contain 1-normal NaOH for coding the gas and neutralizing most of the chlorine/chlorides present in the gas streams. The third impinger was empty and served as a spray trap. The fourth impinger contained silica gel to remove traces of water prior to the dry test meter. Since no trace metals were expected to be present in the gas streams, no analyses were carried out on the impinger contents.

The HVOSS sampling train was cleaned after each sample by following a modified Level I procedure. The probe and probe tip were rinsed with 1:1 $CH_2Cl_2:CH_3OH$ into an amber glass bottle. The XAD-2 resin sorbent trap was cleaned as shown in Figure C-4.

c. High Molecular Weight Hydrocarbons ($>C_6$) - Porus Polymer Type

The high molecular weight hydrocarbons were collected using a porous polymer collection technique to trap and concentrate the materials for GC/MS analysis in the laboratory.

The organic vapors and hydrocarbons were trapped on Porapak Q and Porapak N resins. The sampling equipment used for collecting Porapak tube samples is shown in Figure C-5. The metal cylinder was evacuated to a low pressure using a good vacuum pump. The

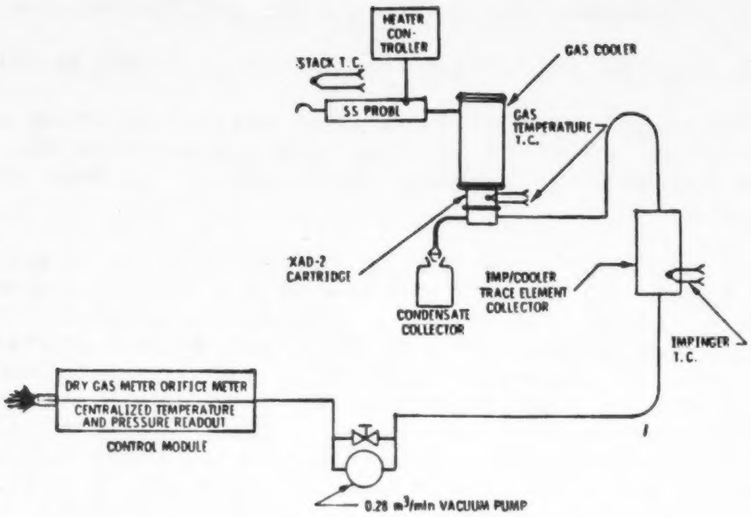
HEATER CON-TROLLER
STACK T.C.
SS PROBE
GAS COOLER
GAS TEMPERATURE T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
0.28 m^3/min VACUUM PUMP

Figure C-2. High volume organic sampling system.[1]

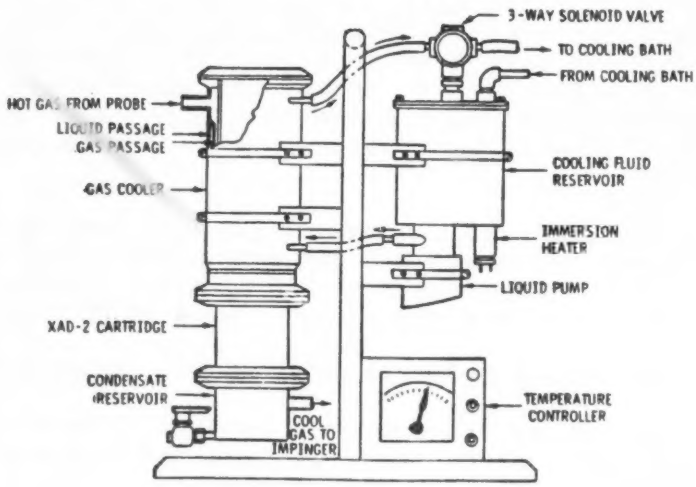
3-WAY SOLENOID VALVE
TO COOLING BATH
FROM COOLING BATH
HOT GAS FROM PROBE
LIQUID PASSAGE
GAS PASSAGE
GAS COOLER
COOLING FLUID RESERVOIR
IMMERSION HEATER
LIQUID PUMP
XAD-2 CARTRIDGE
CONDENSATE RESERVOIR
COOL GAS TO IMPINGER
TEMPERATURE CONTROLLER

Figure C-3. XAD-2 sorbent trap module.[1]

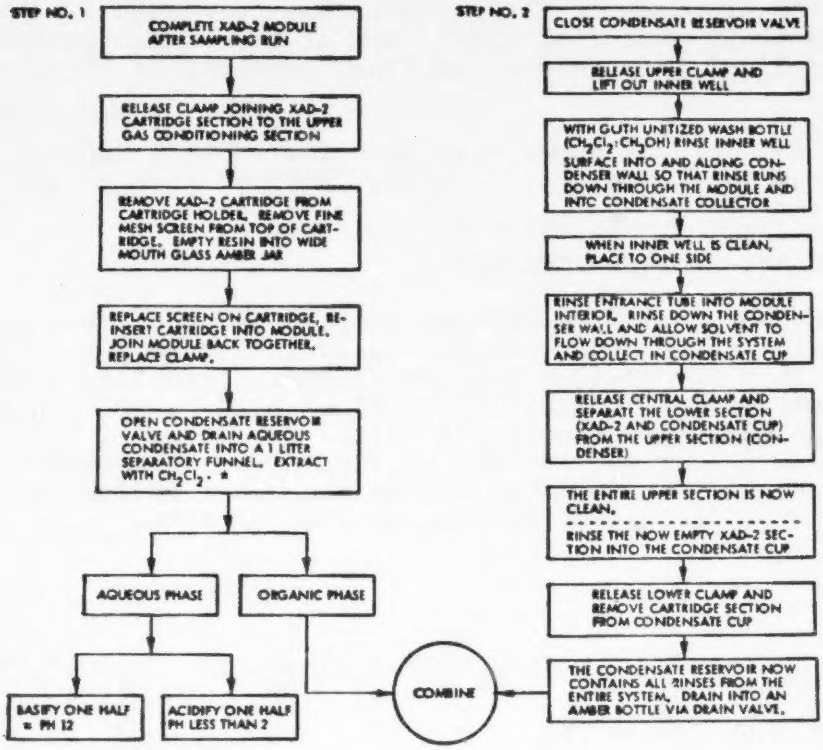
STEP NO. 1
COMPLETE XAD-2 MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING XAD-2 CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE XAD-2 CARTRIDGE FROM CARTRIDGE HOLDER. REMOVE FINE MESH SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO WIDE MOUTH GLASS AMBER JAR
REPLACE SCREEN ON CARTRIDGE, REINSERT CARTRIDGE INTO MODULE. JOIN MODULE BACK TOGETHER. REPLACE CLAMP.
OPEN CONDENSATE RESERVOIR VALVE AND DRAIN AQUEOUS CONDENSATE INTO A 1 LITER SEPARATORY FUNNEL. EXTRACT WITH CH_2Cl_2. *
AQUEOUS PHASE
ORGANIC PHASE
BASIFY ONE HALF ≈ PH 12
ACIDIFY ONE HALF PH LESS THAN 2
COMBINE
STEP NO. 2
CLOSE CONDENSATE RESERVOIR VALVE
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
WITH GUTH UNITIZED WASH BOTTLE (CH_2Cl_2:CH_3OH) RINSE INNER WELL SURFACE INTO AND ALONG CONDENSER WALL SO THAT RINSE RUNS DOWN THROUGH THE MODULE AND INTO CONDENSATE COLLECTOR
WHEN INNER WELL IS CLEAN, PLACE TO ONE SIDE
RINSE ENTRANCE TUBE INTO MODULE INTERIOR. RINSE DOWN THE CONDENSER WALL AND ALLOW SOLVENT TO FLOW DOWN THROUGH THE SYSTEM AND COLLECT IN CONDENSATE CUP
RELEASE CENTRAL CLAMP AND SEPARATE THE LOWER SECTION (XAD-2 AND CONDENSATE CUP) FROM THE UPPER SECTION (CONDENSER)
THE ENTIRE UPPER SECTION IS NOW CLEAN.
RINSE THE NOW EMPTY XAD-2 SECTION INTO THE CONDENSATE CUP
RELEASE LOWER CLAMP AND REMOVE CARTRIDGE SECTION FROM CONDENSATE CUP
THE CONDENSATE RESERVOIR NOW CONTAINS ALL RINSES FROM THE ENTIRE SYSTEM. DRAIN INTO AN AMBER BOTTLE VIA DRAIN VALVE.

Figure C-4. Sample handling and transfer--XAD-2 module.[1]

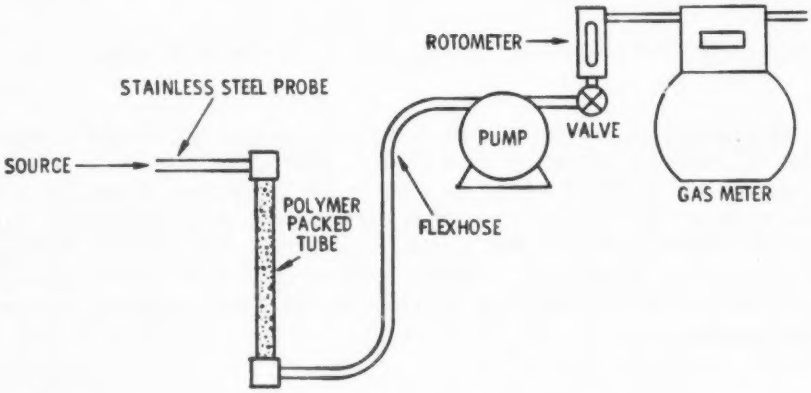
ROTOMETER
STAINLESS STEEL PROBE
SOURCE
PUMP
VALVE
GAS METER
POLYMER PACKED TUBE
FLEXHOSE

Figure C-5. Porous polymer vapor sampling method.

evacuated cylinder was connected to a sample probe and the Porapak tube. The temperature and pressure of the cylinder were noted, and the stopcock in the cylinder was opened to admit a sample for a known period of time. The stopcock was then shut off, and the final temperature and final pressure of the cylinder were noted.

The ends of the Porapak tubes were then sealed off, and the tubes were stored at ice temperatures during shipment back to MRC for GC/MS analysis.

2. CHLORINE AND HYDROGEN CHLORIDE

Chlorine and hydrogen chloride were sampled as chloride using an impinger train system shown schematically in Figure C-6. The system consisted of a Teflon line serving as a sampling probe, three midget impingers containing 10 ml of 0.1N $NaHSO_3$, an empty impinger, a plug of glass wool and silica gel, a pump, a flowmeter, and a dry test meter. The impingers were immersed in an ice-water bath during sampling, and samples were collected at known flow rates for known variable periods of time.

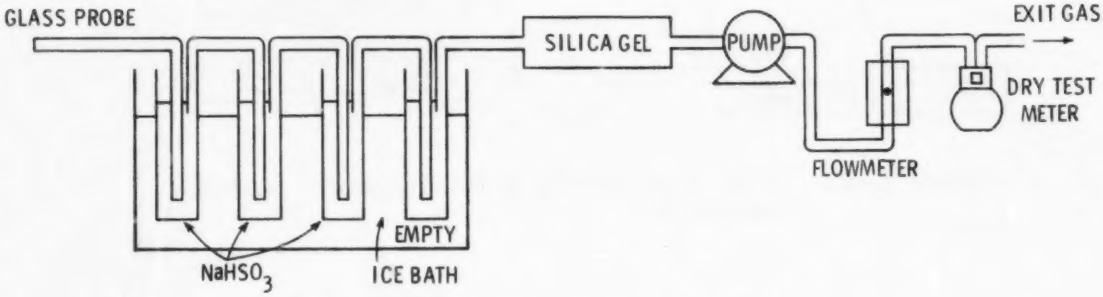

Figure C-6. Chlorine/chloride sampling train.

After sample collection, the first two impinger contents were transferred to a 100 ml sample bottle. The contents of the third and fourth impingers were transferred into another bottle. All glassware, including the empty impinger, were rinsed with three portions of 0.1N $NaHSO_3$ and the rinsings were added to the sample bottle containing its sample. These bottles were then sealed and stored at ice-temperature during shipment to the Dayton Laboratory for subsequent analysis.

APPENDIX D

ANALYTICAL PROCEDURES

The analysis program was carried out both in the field and at the MRC Dayton Laboratory. Field analysis included C_1 to C_6 hydrocarbons by portable gas chromatography with flame ionization detectors (FID). Higher molecular weight organics (C_7 and higher), chlorine, and hydrogen chloride were analyzed in the laboratory. In addition to the C_1 to C_6 field analysis, bag samples were also brought back to the MRC laboratories for GC/MS analysis.

1. LOW MOLECULAR WEIGHT HYDROCARBONS

Low molecular weight hydrocarbons and chlorinated hydrocarbons were analyzed at the plant site employing an Analytical Instrument Development Inc., (AID) Model 511 portable gas chromatograph with a flame ionization detector. For the C_1 to C_3 hydrocarbons, a 1.8 m by 3.2 mm stainless steel column packed with Chromosorb 102 was operated isothermally at an oven temperature of 135°C. For the C_1 and C_2 chlorinated hydrocarbons, a 1.8 m by 3.2 mm stainless steel column packed with 10% FFAP on 80/100 mesh Chromosorb W HP column (suggested by the National Institute of Occupational Safety and Health [NIOSH]) was employed.

The flame ionization detector (FID) rather than electron capture detector (EC) was used for the analysis of the chlorinated species on the basis that the FID detection limit was below the 1 ppm sensitivity required for all species.

Prior to field analysis of samples, optimization and verification of the chromatographic conditions were conducted. Standard gas mixtures were employed to optimize chromatographic conditions (temperature, flow rates of carrier, hydrogen, and air), and to generate calibration curves for the major species expected in the vent emissions.

2. HIGHER MOLECULAR WEIGHT ORGANIC COMPOUNDS - SASS MODULE

Organic compounds with six and more carbon atoms were collected by the organic module of the SASS train. The analytical scheme for this study involved the analysis of the probe washing, XAD-2 resin, and the XAD-2 organic wash and aqueous condensates. In contrast to the normal SASS train analysis scheme, the entire resin sample was analyzed rather than removing 2-gram portions for inorganic analysis.

At the completion of the field cleanup, the samples included the following:

- Bottles containing the CH_2Cl_2-CH_3OH washings of the probe and probe tip
- XAD-2 resin
- Aqueous condensate from the condensate trap
- Methylene chloride rinse of the resin module

The overall analysis scheme is shown in Figure D-1. The XAD-2 resin was Soxhlet entracted for 24 hours with pentane. The volume was measured, and a portion was removed for GC analysis of the C_7 to C_{16} hydrocarbons. The remaining solution was stored for later combination with the other samples from the run.

The aqueous condensate from the run was extracted with methylane chloride, and this extract was combined with the probe washings and methlene chloride rinse of the module. The volume of these solutions was measured, and a portion, equal to the percentage of the portion removed from the pentane extract of the XAD-2 resin extraction, was removed for C_7 to C_{16} analysis. The remaining solution, representing the source percentage of the total as the remaining pentane solution of the extraction total, was combined with the pentane extraction solution. The resulting solution was reduced in volume in a rotovap and then further reduced in volume in the Kuderna-Danish apparatus. Ten milliliters of hexane were added to the apparatus and the volume was reduced to 2 ml. The hexane addition and volume reduction were repeated two more times in order to effect a solvent exchange (methylene chloride replaced with hexane). The resulting hexane solution was diluted to 10 ml. Five milliliters of this solution were evaporated to dryness in order to obtain a weight of the residue. The remaining 5 ml of the solution was analyzed by GC/MS to identify and quantify the components.

3. HIGH MOLECULAR WEIGHT HYDROCARBONS - POROUS POLYMER TUBE

Samples collected by the porous polymer tubes were analyzed at MRC's Dayton Laboratory using combined gas chromatography/mass spectrometry. The porous polymer tubes were thermally desorbed prior to GC/MS analysis. The porous polymer tubes are designed to be directly interfaceable with a gas chromatograph. Desorption of the collected species was initiated using carrier flow and elevated temperature directly onto the analytical column of the gas chromatograph. Assuming air flow rates of 2 ℓ/min and a

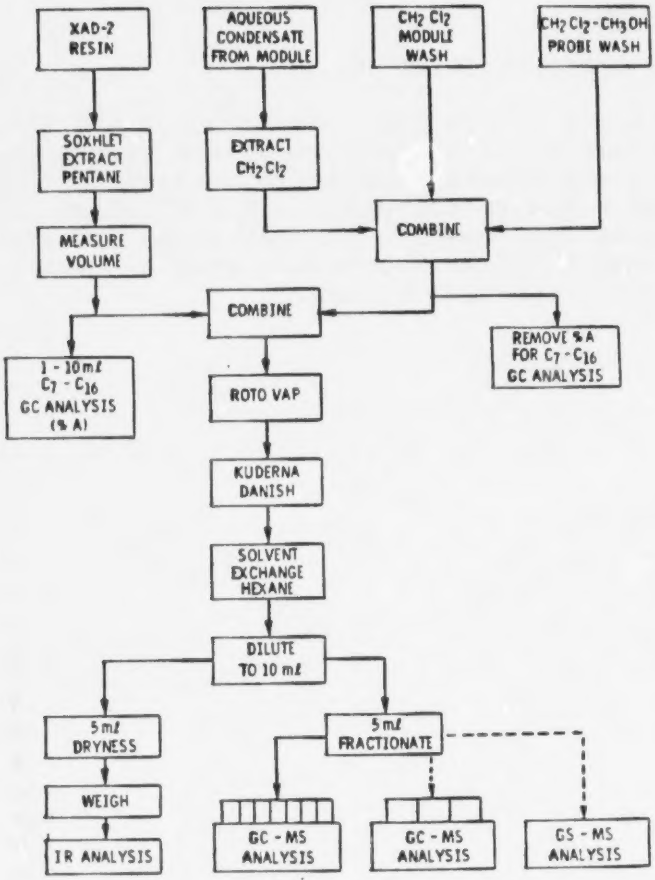
XAD-2 RESIN
AQUEOUS CONDENSATE FROM MODULE
CH2 Cl2 MODULE WASH
CH2 Cl2 - CH3 OH PROBE WASH
SOXHLET EXTRACT PENTANE
EXTRACT CH2 Cl2
COMBINE
MEASURE VOLUME
COMBINE
REMOVE % A FOR C7 - C16 GC ANALYSIS
1 - 10 ml C7 - C16 GC ANALYSIS (% A)
ROTO VAP
KUDERNA DANISH
SOLVENT EXCHANGE HEXANE
DILUTE TO 10 ml
5 ml DRYNESS
5 ml FRACTIONATE
WEIGH
IR ANALYSIS
GC - MS ANALYSIS
GC - MS ANALYSIS
GS - MS ANALYSIS

Figure D-1. Analysis flow scheme for organic compounds C_6 and above.

10-minute sampling time, components present at 0.5 µg/m^3 in the ambient air were measured using a flame ionization detector capable of detecting 10 µg.

The porous polymer tube was connected to the inlet system of the GC/MS so that the carrier gas passed through the tube in a direction reverse to that of the original sampling flow. The collected tube was heated over its entire length, and the desorbed gases were swept into the instrument. As in any GC-related method, the choice of the analytical column and conditions determined the separation possible for the individual compounds collected in the tubes. Mass spectra were recorded for each peak when it was suspected that several components occurred at the same retention times, additional mass data were obtained. Mass data provided an identification of the compounds present, and the GC data quantified these compounds.

4. CHLORINE AND HYDROGEN CHLORIDE

Chloride ion analysis of the impinger solution was executed employing the Dionex Model 10 analytical ion chromatograph. A calibration curve was generated using a potassium chloride standard solution from 1 ppm to 500 ppm. A 0.1 ml aliquot of the sample was injected into the ion chromatograph and read according to peak height, and a linear regression equation was used to interpolate the concentration values.

APPENDIX E

SAMPLE CALCULATIONS

In this appendix, sample calculations are shown in the following subsections for: 1) volume of gas sampled, 2) percent moisture, 3) calculation of percent error bound, 4) concentrations of chlorine/chloride in stack gases, 5) concentrations of hydrocarbons determined by collector tube method, 6) concentrations of GC/FID determined components in Tedlar bag samples, and 7) calculation of stack gas flow rates.

1. VOLUME OF GAS SAMPLED

The gas volume sampled was determined by adjusting the volume of gas metered with respect to the pump leak rate and the standard conditions of 20°C and 760 mm Hg. Thus,

$$\mathrm{VMS} = \frac{17.71[\mathrm{VM} - \mathrm{LR(MIN)}]\mathrm{PB}}{(\mathrm{TM} + 460)} K_1 \qquad \text{(E-1)}$$

where VMS = volume of dry gas sampled at standard condition, m^3
VM = volume of dry gas sampled at meter conditions, ft^3
LR = leak rate of pump at meter conditions, ft^3/min
MIN = number of minutes sampled
PB = absolute barometric pressure, in. Hg
TM = average meter temperature, °F
$K_1 = 2.8317 \times 10^{-2}\ m^3/ft^3$

and 460 and 17.71 are constants to adjust degrees Fahrenheit to absolute temperature and to adjust to standard conditions.

Example: Run 1 Scrubber Outlet

VM = 630.511

LR = 0.08

MIN = 145

PB = 29.84

TM = 84°F

$$VMS = \frac{17.71[630.511 - 0.08 \times 145]29.84}{(84 + 460)} \times 2.8317 \times 10^{-2}$$

$$= 601.24 \times 2.8317 \times 10^{-2}\ ft^3 = 17.03\ m^3$$

2. PERCENT MOISTURE

Percent moisture was determined by calculating the volume of water vapor, at standard conditions that the total water volume collected would comprise, calculated as the mole fraction of water vapor in the gas stream and changed to percent. Thus,

$$VL = V_1 + V_2 + V_3 + V_4 + V_5 \qquad (E\text{-}2)$$

$$VW = (0.0474)VL \qquad (E\text{-}3)$$

$$MW = \frac{VW}{VWSF + VW} \qquad (E\text{-}4)$$

$$\%M = 100MW \qquad (E\text{-}5)$$

where VL = total volume of water collected, ml

V_1 = volume of water collected in impinger 1 (final minus initial volume), ml

V_2 = volume of water collected in impinger 2 (final minus initial volume), ml.

V_3 = volume of water collected in impinger 3 (final minus initial volume), ml.

V_4 = weight of water collected in silica gel (final minus initial weight), g[a]

V_5 = volume of aqueous condensate in condenser, ml

0.0474 = constant to adjust to volume of water vapor at standard condition

VMSF = volume of dry gas sampled at standard conditions, ft^3

VW = volume of water vapor at standard conditions, ft^3

MW = mole fraction of water vapor

%M = percent moisture

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[a] 1 gram of water equals approximately 1 millileter of water.

Example: Run 1 Scrubber Outlet

$V_1 + V_2 = 30$ mℓ

$V_3 + V_4 = 143.5$ g

VL = 173.5

VW = 0.0474 x 173.5 = 8.22

VMSF = 601.24

$$MW = \frac{8.22}{601.24 + 8.22} = 1.33 \times 10^{-2}$$

%M = 1.33%

3. CALCULATION OF PERCENT ERROR BOUND

Percent error bounds, ±% are calculated as:

$$\pm\% = \left[\frac{s(t)}{\sqrt{N}}\right]\left(\frac{1}{\bar{x}}\right) 100 \qquad \text{(E-6)}$$

where s = standard deviation

t = value from statistical tables for student "t" distribution using the 95% confidence level, and the degrees of freedom, "f"

f = N-1

N = number of measurements

$\bar{x}$ = average of measurements

Example: Run 1 Scrubber Outlet

s = 20.9

$\bar{x}$ = 66.2

N = 3

t = 4.303

$$\pm\% = \left(\frac{20.9 \times 4.303}{\sqrt{3}}\right)\left(\frac{1}{66.2}\right) 100 = 78.6\%$$

4. CONCENTRATIONS OF CHLORINE/CHLORIDE IN STACK GASES

Analytical results for the chlorine/chloride analysis were reported as grams of chloride collected in the impingers.

Determining concentrations of chlorine/chlorides in gas streams involves the following:

- Volume of gas sampled at standard conditions.
- Grams per milliliter of chlorine/chloride in blank.
- Grams per milliliter of chlorine/chloride in sample.
- Grams per milliliter of chlorine/chloride in stack gas.
- Grams of chlorine/chloride in stack gas
- Grams per cubic meter of chlorine/chloride in stack gas.

a. Volume of Gas Sampled, VMS

$$\text{VMS} = \frac{17.71\ \text{PB(VM)}}{\text{TM} + 460} \qquad \text{(E-7)}$$

where TM = average meter temperature, °F
PB = absolute barometric pressure, in. Hg
VM = volume of gas sampled at meter conditions, ft^3
VM = FR x M
FR = flow rate, ft^3/min
M = sampling time, min

b. Chlorine/chloride in Stack Gas, grams/m^3

Chlorine/chloride

$$= \frac{\left[\dfrac{\text{grams chloride in sample}}{\text{volume of sample (m}\ell\text{)}} - \dfrac{\text{grams chloride in blank}}{\text{volume of blank (m}\ell\text{)}}\right] \times \text{volume of sample (m}\ell\text{)}}{\text{VMS ft}^3 \times \dfrac{0.0283\ \text{m}^3}{\text{ft}^3}}$$

Example: Run 1 Scrubber Inlet

Grams of chloride in sample = 1.66 gm
Volume of sample = 116 mℓ
Grams of chloride in blank = 6.0×10^{-3} gm
Volume of blank = 61 mℓ
VMS = 1.06 ft^3

Chlorine/chloride $= \dfrac{\left[\dfrac{1.66}{116} - \dfrac{6.0 \times 10^{-3}}{61}\right] 116}{1.25 \times 0.0283}\ \text{g/m}^3$

$= 46.7\ \text{g/m}^3$

5. CONCENTRATIONS OF GC/FID DETERMINED COMPONENTS IN TEDLAR BAG SAMPLES

Low molecular weight hydrocarbons ($<C_6$) were analyzed in the field using GC/FID analysis. Results were reported in ppm by weight. To obtain concentrations in grams per cubic meter the following conversions were involved:

$$\text{ppm (weight)} = \frac{\dfrac{\mu g}{g} \cdot \dfrac{g}{g\ \text{mole}} \cdot \dfrac{10^{-6}\ g}{\mu g}}{\dfrac{22.4\ \ell}{g\ \text{mole}} \cdot \dfrac{0.001\ m^3}{\ell}}$$

Example: Run 1 Scrubber Outlet

Detected 200 ppm CH_4 equivalents

$$\text{Concentration} = \frac{\dfrac{200\ \mu g}{g} \cdot \dfrac{16\ g}{g\ \text{mole}} \cdot \dfrac{10^{-6}\ g}{\mu g}}{\dfrac{22.4\ \ell}{g\ \text{mole}} \cdot \dfrac{0.001\ m^3}{\ell}}$$

$$= \frac{200 \cdot 16 \cdot 10^{-6}}{22.4 \cdot 0.001} \frac{g}{m^3} = 1.4 \times 10^{-1}\ g/m^3$$

6. CONCENTRATION OF THE GC/MS DETERMINED COMPONENTS OF THE HVOSS SAMPLE

The component results were reported as the total amount of compound present in milligrams in the sample submitted for GC/MS analysis. This sample represented 99.5% of the material collected, because 0.5% was removed for GC analysis for C_7 - C_{16} hydrocarbons. Therefore, to obtain total weight of sample collected, the steps required include the following:

- Subtract the amount of compounds present in the blank from the amount of compounds present in the sample

- Add 1% to the total to adjust for the removal of sample for C_7 - C_{16} analysis

- Divide the amounts of material collected by the volume of gas sampled to obtain the concentration in g/ft^3

- Correct the concentration units to grams per cubic meter

Example: Run 1 Scrubber Outlet - C_{16} - C_{36} Aliphatics

Amount of C_{16} - C_{36} aliphatics detected = 20.146 mg

Amount of C_{16} - C_{36} aliphatics in blank = 13.222 mg

Therefore, amount of C_{16} - C_{36} aliphatics in sample = 6.924 mg

Correction for 0.5% removed for C_7 - C_{16} analysis = 0.035

Total amount of C_{16} - C_{36} aliphatics collected = 6.959 mg

Volume of gas sampled at STP = 17.02 m^3

Therefore concentration of C_{16} - C_{36} aliphatics in stack = 0.41 mg/m^3

7. CONCENTRATION OF C_7 THROUGH C_{16} (ALKENES) DETERMINED BY GC FROM HVOSS SAMPLE

The concentration of the C_7 - C_{16} hydrocarbons detected in the sample were reported as milligrams of material present in the sample in a given volume submitted for GC analysis. This sample represented only 0.5% of the total sample collected, because 99.5% was sent for GC/MS analysis. Therefore to obtain the total weight of sample collected the required steps include the following:

- Subtract the amount of material present in the blank from the amount present in the sample
- Add 99% to the total to adjust for the removal of a sample for GC/MS analysis
- Perform the above steps for both XAD-2 resin extract and for combined organic phases
- Add the results for both XAD-2 resin extract and for combined organic phases
- Divide the amounts of material collected by the volume of gas sampled to obtain the concentration in g/ft^3
- Correct the concentration units to grams per cubic meter

8. STACK GAS FLOW RATE

Stack gas data were obtained by taking a preliminary velocity traverse across the duct carrying the stack gases. At each traverse point, the velocity had (Δ PS) and stack temperature were determined.

The velocity of the stack gas was determined using the following equation.

$$VS = 85.48 \times CP \sqrt{\frac{TS + 460}{PS \times MS}} \left(\sqrt{\Delta p}\right)_{\text{average}} \qquad \text{(E-8)}$$

where VS = stack gas velocity, ft/s

CP = pitot tube coefficient

TS = average temperature of stack, °F

PS = absolute pressure of stack gas, in. Hg

MS = molecular weight of stack gas, lbs/lb mole

$(\sqrt{\Delta p})_{\text{average}}$ = average of square root of velocity head, $(\text{in. } H_2O)^{1/2}$

The volumetric flow rate (SCFM) was then determined using the equation:

$$Qs = 60 \left[1 - (M \times 10^{-2})\right] VS \times A \times \left(\frac{530}{TS + 460}\right) \times \left(\frac{PS}{29.92}\right) \qquad \text{(E-9)}$$

where M = percent moisture

A = area of stack, ft^2

Example: Run 1 Stack Gas Velocity Calculation - Scrubber Outlet

$M = 1.35$

$CP = 0.75$

$A = 0.35$

$TS = 75°F$

$PS = 29.88$

$(\sqrt{\Delta p})_{\text{average}} = (0.98)$

$$VS = 85.48 \times CP \sqrt{\frac{TS + 460}{PS \times MS}} \left(\sqrt{\Delta p}\right)_{\text{average}}$$

$$\therefore VS = 85.48 \times 0.75 \sqrt{\frac{75 + 460}{29.88 \times 28.8}} (0.98)$$

$$= 49.54 \text{ ft/s}$$

Also $Qs = 60\ [1 - (M \times 10^{-2})]\ VS \times A \times \frac{530}{TS + 460} \times \frac{PS}{29.92}$

$= 60\ [1 - (1.35 \times 10^{-2})]\ 49.54 \times 0.35 \times \frac{530}{75 + 460}$

$\times \frac{29.88}{28.92}$

= 1015.32 ft3/min

$= 60919\ ft^3/hr$

$= 60919\ \frac{ft^3}{hr} \times \frac{0.0283\ m^3}{ft^3}$

$= 1724\ m^3/hr$

CONVERSION FACTORS AND METRIC PREFIXES[78]

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius (°C)	degree Fahrenheit	$t^\circ_F = 1.8\ t^\circ_C + 32$
gram/second (g/s)	pounds/hour	7.936
joule (J)	calorie	2.388×10^{-1}
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.204
kilogram/meter^3 (kg/m^3)	pound/foot^3	6.243×10^{-2}
kilometer^2 (km^2)	mile^2	3.860×10^{-1}
meter (m)	foot	3.281
meter^3 (m^3)	feet^3	3.531×10^{1}
metric ton	pound-mass	2.205×10^{3}
metric ton	ton (short, 2,000 lb-mass)	1.102
pascal (Pa)	atmosphere	9.869×10^{-6}
pascal (Pa)	torr (mm Hg, 0°C)	7.501×10^{-3}
pascal (Pa)	pound-force/inch^2 (psi)	1.450×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
mega	M	10^6	1 MJ = 1×10^6 joules
kilo	k	10^3	1 kPa = 1×10^3 pascals
micro	μ	10^{-6}	1 μg = 1×10^{-6} gram

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[78] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^{\varepsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.